



**ARCTIC
RESPONSE
TECHNOLOGY**
OIL SPILL PREPAREDNESS

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**RESEARCH INVESTIGATIONS INTO HERDER FATE,
EFFECTS AND WINDOWS-OF-OPPORTUNITY**



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LIST OF ABBREVIATIONS, SYMBOLS AND ACRONYMS

Term Abbreviation or Symbol

Alaska Clean Seas	ACS
Alaska Regional Response Team	ARRT
Arctic and Marine Oilspill Program	AMOP
American Petroleum Institute	API
Bureau of Safety and Environmental Enforcement	BSEE
Crude Oil Flammability Apparatus	COFA
Environmental Protection Agency (U.S.)	EPA
Minerals Management Service	MMS
National Contingency Plan	NCP
International Association of Oil & Gas Producers	IOGP
Oil and Hazardous Material Simulated Test Tank	OHMSETT
Polynuclear aromatic hydrocarbons	PAHs
Polychlorinated biphenyls	PCBs
Particulate matter	PM
Volatile organic compounds	VOCs

GLOSSARY OF KEY TERMS

Acute Toxicity is a measure of the potential of a material (e.g., oil, chemicals) to cause adverse effects in an organism after only a short period of exposure (generally less than 4 days) relative to its life cycle length.

Ambient Conditions are those in an environment, such as ambient temperature, humidity, etc. For example, if an oil slick is at or above the temperature of its flash point, the slick will ignite rapidly and easily. If the ambient temperature is below the flash point for the spilled oil, the slick may be difficult to ignite.

API Gravity (API) is a scale for measuring fluid specific gravities based on an inverse relationship with specific gravity (SG). This scale was primarily developed to expand the scale for specific gravity so that larger values are used. An oil with a low specific gravity (e.g., gasoline; SG = 0.73) will have a high API gravity (API = 62).

$$\text{API gravity} = (141.5/\text{SG at } 15.5^{\circ}\text{C}) - 131.5$$

Aromatic Hydrocarbons are composed solely of carbon and hydrogen atoms in various arrangements that include at least one benzene ring. Aromatic hydrocarbons give oil its smell.

Average flame height is defined as the steady flame height over time that is at least present 60% of the time.

Barrel (bbl) is equal to 42 United States gallons (or 159 litres) at 15.5°C.

Barbule Amalgamation Index (AI) is a method developed to quantify the clumping of barbules as a result from exposure to oil, herders etc.

Barbs are lateral branches of the central shaft (rachis) of the feather and provide the primary structure of a feather. Each barb is divided into branches that are called barbules. Barbs and barbules form an interlocking and strong and flexible surface called a vane. The barbs and barbules are attached to another by hooks. The distal barbules (those extending off the barb toward the feather tip) bear tiny hooklets that fit into grooves on the proximal barbules (those extending off the barb toward the quill) of the next higher barb.

Barbules (distal and proximal) see barbs

Benthic pertains to the bottom of a body of water or organisms which live on or near it.

Benzene, toluene, ethyl benzene and xylene (BTEX) compounds are volatile organic compounds which are present in light refined products and crude oils. Their presence after a burn would indicate incomplete combustion of some of the oil.

Biodegradation is transformation of a substance into new compounds through biochemical reactions or the actions of microorganisms such as bacteria.

Bioaccumulation is the accumulation of a chemical in an organism.

Bio concentration Factor (BCF) is the concentration of a chemical in the test organisms divided by the concentration of the chemical in the surrounding medium after a specified exposure time (as opposed to equilibrium BCF).

Body residue is the concentration of a chemical in an organism's tissue.

Boilover is the drastic burning of the fuel owing to water boiling and splashing under the fuel layer, which prompts into an explosive burning of the fuel, sharp increase in burning rate and abrupt increase of flames. This phenomenon is also known as thin-layer boilover and is defined by: its onset of water boiling nucleation at the water/fuel interlayer that takes place at a constant temperature, that is above the saturation temperature of the water (approximately 120 °C; and its intensity.

Booms are floating barriers used for the collection, diversion, deflection, and containment of spreading liquids.

Brackish is an intermediate salinity range for water bodies where the portion of salt water is greater than fresh (0.50 to 17.00 parts per thousand).

Brash Ice is defined as accumulations of floating ice fragments not more than 2 m across. Brash ice is common between colliding floes or in regions where pressure ridges have collapsed.

Broken Ice is an older term used to describe an ice sheet that is not continuous. It has been replaced by the more descriptive terms pack ice, drift ice, etc.

Burning Efficiency is usually expressed as the percent reduction in original oil weight following combustion. It is a function of three main factors: initial slick thickness; thickness of residue at the extinction of the burn; and the aerial coverage of the flame.

Burn Residue is the unburned oil or incomplete combustion products remaining on land, water, snow or ice surface after a fire is extinguished. Residues can range from brittle stiff, taffy-like material, to a liquid similar to the original oil.

Calamus is the base of the feather.

Centipoise (cP) a unit of measurement for dynamic viscosity.

Centistoke (cSt) a unit of measurement for kinematic viscosity.

Chemical Treating Agents are products used in treating oil spills, including dispersants, bioremediation agents (nutrient additions), herding agents, emulsion treating agents, solidifiers, elasticity modifiers, surface washing agents, and miscellaneous oil spill control agents.

Chronic Toxicity is a measure of potential of a material to cause an adverse effect in organism exposed to the contaminant for a significant portion of its life cycle.

Combustion By-Products include the smoke plume constituents and any incomplete burn combustion products remaining after a burn is extinguished (residue).

Containment is the use of boom, herding agents, natural barriers on land, or ice, to constrain and/concentrate the oil slick.

Controlled Burn is combustion that is started and stopped by human intervention.

Convective Motion is flow of a fluid induced by temperature differences.

Copepods are a group of pelagic crustaceans found in the sea and nearly every freshwater habitat.

Density of the oil is a measure of how heavy a specific volume of a solid, liquid, or gas is in comparison to water. The greater the density of a resultant burn residue, the more likely it is to sink.

Detergent is a surfactant or a mixture of surfactants.

Dichloromethane (DCM) is an organic, highly volatile and colourless liquid chemical. It is typically used as a solvent or cleaning agent.

Dispersion is a process in which a compound (e.g. oil, herder) is mixed into a continuous phase (e.g. the sea)

Dissolving / Dissolution is a process in which a compound (e.g. oil or herder) passes into solution in a liquid (e.g. the sea)

EC₅₀ or EC50 is the concentration of a chemical that causes 50 percent effect to the test organism over a stated period of time. Length of exposure is usually 24 to 96 hours.

Effectiveness / Efficacy is the ability to produce the desired outcome

Emulsification is the process of mixing water droplets into the spilled oil forming highly viscous mixtures that have reduced weathering capabilities and are usually more difficult to burn, disperse, and mechanically recover.

Emulsion for spill response purposes is the suspension of water in an oil slick which then alters its appearance, behavior, fate, and impacts recovery and treatment options. Water-in-oil emulsions may contain 20% - 80% water. Emulsions may be temporary or permanent.

Encounter Rate refers to the amount of oil which comes into contact with a containment and recovery device (e.g. boom, skimmer or sorbents) or is treated (i.e. burned or dispersed) over a given period of time.

Evaporation is the preferential transfer of light- and medium-weight components of the oil from the liquid phase to the vapour phase. Evaporation is typically the most dominant weathering process (oil type and spill location dependent).

Fate refers to what happens to a compound after it has been released to the environment

Fire Diameter is the horizontal distance from one side of a fire to the opposite side, through the centre of the fire.

Fire Point is the temperature of a fuel at which it will continue to burn for at least 5 seconds after ignition by an open flame.

Flammability limit is the range of concentration of flammable vapours in air that will ignite.

Flash Point is the lowest temperature at which the vapour of a flammable liquid will ignite in air. The flash point is generally lower than the temperature needed for the liquid itself to ignite. A substance may ignite briefly, but vapour may not be produced at a rate to sustain a fire. In general a fire points can be assumed to be about 10°C higher than the flash point for a given material.

Fresh / Freshwater is a classification of waterbody by its low salinity less than 0.5 parts per thousand (ppt).

GC-MS in SIM mode is an instrument method where the machine is programmed to only look for specific mass ions which increase the sensitivity

Global mass burning rate, is the global mass rate of liquid fuel vaporised and burnt or the mass lost per unit time of a specimen (crude oil) burning, it is expressed in kg/s or g/s and is denoted as \dot{m}_{global} .

Heat Flux is the total amount of heat radiated, convected and conducted away from a fire per unit time.

Herding Agent is a product which contracts a liquid (in this case an oil slick) on a water surface by exerting a higher spreading pressure than the oil slick.

Hydrophilic / Hydrophobic is the terms defining a compounds affinity for and against water, respectively

Ice-affected waters are those that have ice in some form on their surface.

Ignition Sources/Igniters are devices designed to provide heat to a material and increase its temperature to its Fire Point and provide an ignition source. Commonly used ignition devices include propane or butane torches, gelled fuel with an attached flare, diesel-soaked rags or sorbents, helicopter-slung gelled fuel (Helitorch), and road flares.

Ignitable Thickness means in general, the thickness of oil necessary to generate sufficient vapours to enable ignition.

Immiscible Liquids do not mix with each other.

In-Situ Burning (ISB) is the controlled combustion/burning of spilled oil in place such that the petroleum hydrocarbons are predominantly converted to CO₂ and water which are released to the atmosphere. See also Controlled Burning.

Interfacial Tension is the tendency of a liquid surface, in contact with an immiscible liquid, to contract. The imbalance of forces at the liquid-liquid interface is due to the difference in molecular forces in the two immiscible liquids.

Lipids are organic compounds that are insoluble in water, and soluble in alcohol and ether: lipids comprise the fats and other esters with analogous properties and constitute, with proteins and carbohydrates, the chief structural components of living cells

LC₅₀ or LC50 is the concentration of a product that causes 50 percent mortality to the test organism over a stated period of time. Length of exposure is usually 24 to 96 hours.

Marine or Saltwater is a classification of waterbody based on salinity. . It is sometimes used synonymously with ocean, but reflects a broader salinity range from 17 parts per thousand and up.

Marine Environment is characterized or described as the oceans, seas, bays, estuaries, and other major water bodies and the related processes also at species and genetic level

Microbial Degradation is a naturally occurring process where micro-organisms consume petroleum hydrocarbons as a food source. See biodegradation.

Miscible is the ability of one liquid to be mixed at any ratio, into a second liquid without separation of the two liquids.

Monolayer is defined as a single layer of atoms or molecules absorbed on a surface

Natural Dispersion is the process of breaking waves forcing oil droplets into the water column, which can result in at least a portion of the droplets small enough to remain in the water.

NEBA is an acronym for Net Environmental Benefit Analysis. It is the comparison of environmental and socio-economic outcomes of selected spill scenarios using various response

options against a baseline, whose results are used in contingency planning stages and during a response to inform decision-making as to those options with the least negative effects. In this context, the baseline for comparison is slick monitoring and observation only, while response options can include mechanical only, mechanical and dispersants, dispersants only, ISB, etc. The NEBA process is typically used when a response option other than mechanical recovery alone, and especially for on-water spill scenarios, is desired.

Niskin Bottle is a water sampling device made of plastic or metal that can be opened/closed in both ends.

No Observed Effect Concentration (NOEC) is the highest tested concentration that causes no discernible effect.

No Observed Effect Slick Thickness (NOEST) is the highest slick thickness that causes no discernible effect.

Ohmsett is the National Oil Spill Response Test Facility, located in Leonardo, New Jersey, USA. The name Ohmsett is an acronym for "Oil and Hazardous Materials Simulated Environmental Test Tank"

Oil means oil of any kind of petroleum hydrocarbon, in particular those in liquid form which could be spilled.

Oleophilic means having a strong affinity for oils

Particulates are very small pieces of solid materials (e.g. dusts, soot, fumes) or liquid material (mists, fogs, sprays) that remain suspended in the air long enough to be inhaled.

Particulate Matter refers to particulates with a size range at 10 micrometers in diameter or smaller that are judged to be more easily inhaled and can enter lungs. Particulate matter is often grouped into two categories:

1. PM 10 is a coarser mixture of solid and liquid droplets (up to 10 microns in diameter).
2. PM2.5 are particles less than 2.5 micrometers in diameter are called "fine" particles. These particles are so small they can be detected only with an electron microscope. Sources of fine particles include all types of combustion, including motor vehicles, power plants, residential wood burning, forest fires, agricultural burning, and some industrial processes.

Parts per billion (ppb) is a unit of concentration. One ppb is roughly equivalent to one teaspoon in 5,000,000 litres.

Parts per million (ppm) is a unit of concentration. One ppm is roughly equivalent to one teaspoon in 5,000 litres.

Parts per thousand (ppt) is a unit of concentration. One ppt is roughly equivalent to one teaspoon in 5 litres.

Persistence is a means of defining how crude and refined oil products may remain in the environment. Persistent oils may not be completely removed from an affected environment as a result of weathering processes or clean-up operations.

Photo-Oxidation is the process by which components in an oil are chemically transformed through a photo-chemical reaction (in the presence of atmospheric oxygen) to produce compounds which tend to be both more water soluble and acutely toxic (in the near term) than the parent compounds.

Polynuclear Aromatic Hydrocarbons (PAHs) are a group of hydrocarbons compounds characterized by multiple benzene rings, very low vapour pressures, and relatively low flammability (compared to other compounds found in crude oils). PAHs are found in unburned and burned oil as well as in smoke plumes.

Pour Point is the temperature below which oil will cease to flow in a specified test apparatus and from a spill response perspective means oil is transitioning from a liquid to a solid.

Recovery rates is the extent to which an instrument is able to measure or rediscover a known amount/concentration.

Red cap bottles, is laboratory glass bottles, with a red PBT (with PTFE seal) cap.

Residue is the small amount of burned and unburned oil found on the water surface (or sunken, depending on the density) resulting from an in situ burning operation.

Risk Assessment is the characterization of quantitative or qualitative estimate of risk related to a concrete situation and a recognized hazard.

Salinity is a measure of the relative concentration of salt in seawater, a solution, such as water. Usually measured as parts per thousand (ppt). Ocean water is typically 35-36 ppt.

Sea birds are a group of bird species that lives on or near the sea and use the sea for foraging.

Sheen is a very thin layer of floating oil, less than 0.0003 mm in thickness. Sheen may appear as silver (0.00007 mm), rainbow (0.00015 mm) or gray (0.001 mm), depending on thickness, sheens range in colour from dull brown for the thickest sheens to rainbow, grays, silver, and near-transparency in the case of the thinnest sheens.

Slick is a thin layer of spilled oil.

Slicklet is a very small thin layer of spilled oil.

Solidifier is a product which mixes with oil to turn it into a rubber-like solid.

Soluble / Solubility is the relative ability of one material to dissolve in another. A product is considered "quite soluble" in water if its solubility is greater than 1 ppt. A product is considered "sparingly soluble" in water if its solubility is between 1 ppt and 1 ppm. A product is considered "very sparingly soluble" in water if its solubility is between 1 ppm and 1 ppb. A product is considered "essentially insoluble" in water if its solubility is 1 ppb or less.

Sorbent is any oleophilic material which is used to take up oil through absorption or adsorption. Essentially made from inert and insoluble materials that are used to remove oil and hazardous substances from water through adsorption, in which the oil or hazardous substance is attracted to the sorbent surface and then adheres to it; or by absorption, in which the oil or hazardous substance penetrates the pores of the sorbent material; or a combination of the two.

Specific Gravity (SG) is the ratio of the mass of a material (e.g., oil) to the mass of freshwater, for the same volume and at the same temperature. Most crude oils and refined products have specific gravity values between 0.78 and 1.00. If the SG of an oil is less than the SG for a surface water (freshwater (SG) is = 1.0 at 4°C; seawater (SG) is = 1.03 at 4°C), then the oil will float on the water surface.

Spreading is the dominant transport process for most oil spills, whether on water, on land, or in ice/snow. Spreading occurs due to surface tension and gravity.

Spreading Pressure is the force exerted against a fixed barrier as a liquid is compressed into a smaller surface area.

Stock Solution is a concentrate, which is to be diluted to some lower concentration for actual use

Surface Collecting Agents are those chemical agents which form a surface film to control the layer thickness of oil. See herding agent.

Surface Tension is the tendency of a liquid surface, in contact with air, to contract due to an imbalance of forces on the molecules in the bulk liquid versus those at the surface in contact with air.

Surfactant, also referred to as surface-active agent, is a chemical which contains both an oil-soluble and water-soluble components

Toxicity is the inherent potential or capacity of a material (e.g., oil, chemicals) to cause adverse effects in a living organism.

Viscosity is the resistance to flow and may be reported in one of two ways for oil spills. Dynamic viscosity (μ) refers to internal friction of a substance (e.g., oil) that is a function of the oil type and temperature and is measured in Centipoise units (cP). The lower the viscosity, the thinner the fluid (e.g., water = 1 cP, molasses = 100,000 cP). Kinematic viscosity (ν) is a given fluids dynamic viscosity divided by its density, is measured in Stoke (St) units and is often reported in centistoke (cSt). Since the density of oil is not too different from water, rough estimates of dynamic and kinematic viscosities are similar.

Volatility is the tendency for the components in a liquid to vapourize.

Volatile organic compounds (VOCs) are a mixture of the lighter, Low Molecular Weight (LMW) hydrocarbons, including benzene. During any spill, the lighter, more volatile components evaporate more quickly, and much slick volume can be lost from within the first 24–48 hours.

Water Column is an imaginary cylinder or box from the surface of the water to the bottom.

Weathering is the process of alteration of physical and chemical properties of a material through natural processes, including spreading, evaporation, dissolution, photo-oxidation, emulsification, sedimentation, and biodegradation.

Window of Opportunity is an interval of time during which conditions are favorable and an opportunity exists for a spill response option to be implemented effectively.

EXECUTIVE SUMMARY

In-situ burning (ISB) offers an effective spill response tool in a variety of ice concentrations. The key to effective ISB is thick oil slicks. In low ice concentrations oil on water can rapidly spread to become too thin to ignite. The focus of herder research for Arctic oil spill response has therefore been on their application in drift ice conditions (1 to 6 tenths ice cover) in which slicks can spread fairly rapidly. Further, herders provide a potential method of enhancing in situ burning in open water conditions. Another potential advantage of herders is the possibility that the entire operation could be carried out using a rapidly deployable platform such as helicopters, or possibly even remote control aircraft, to spray herders on the water around slicks and then ignite the thickened oil with aerially-deployed igniters. This type of totally aerial response could be much faster, more effective, safer and less complicated than conventional icebreaker-based countermeasures in Arctic waters.

Two herding agents, ThickSlick 6535 and OP-40 have been listed on the U.S. EPA National Contingency Plan (NCP) Product Schedule for consideration for use on spills in U.S. waters. ThickSlick 6535 is a blend of 65 volume % sodium monolaurate (Span 20), the surfactant, and 35% 2-ethyl butanol solvent. The active ingredient of ThickSlick 6535 is used as a food additive, in household cleaners as well as in cosmetics, fine fragrances and other toiletries. OP-40 is a proprietary polydimethylsiloxane copolymer compound. Surfactants of the type used in OP-40 are used in household and automotive care products as well as in hair conditioners and skin care products.

The evaluation of herders for approval by the US EPA is based on data from standard laboratory tests which are performed with temperate or tropical species over a period of 1-4 days at temperatures between 15-20 °C . However, the environment and biology in Arctic waters are characterized by low temperatures in surface waters throughout the year, large seasonal variations in solar radiation, high prevalence of sea ice, a unique animal and plant life adapted to the cold climate and life associated to the sea ice, general slow biological processes, short food chains and a high content of lipids (fats) in the organisms (AMAP, 1998). The relative high content of lipids / fats serves partly as an energy reserve to withstand long periods without food and partly as insulation against the cold environment. To reduce the uncertainty from the temperate standard tests with non-Arctic species, toxicity and bioaccumulation of herders was investigated in laboratory tests with high Arctic copepods at Arctic temperatures. Copepods occupy a key function in high Arctic seas as food for fish, seabirds and marine mammals.

No herders have been approved for use in other nations' Arctic waters, thus the data and results from this project provide a basis for performing a robust windows-of-opportunity and environmental risk evaluation of herders for ISB in Arctic seas.

The objective of this multi-project and interdisciplinary research programme was to advance the knowledge of chemical herder environmental fate, effects and performance in order to expand the operational utility and environmental assessment of ISB in open water and in ice-affected waters with drift ice conditions. This project was undertaken by two main research groups:

- SL Ross Environmental Research Ltd as prime contractor carried out the research on the windows of opportunity for herder use at their laboratory in Ottawa, Ontario, Canada and at the US Army Corps of Engineers Cold Regions Research and Engineering Laboratory (CRREL) in New Hampshire, U.S.A.

- DCE - Danish Centre for Environment and Energy, at Aarhus University in Denmark performed the herder effects research in co-operation with the Technical University of Denmark (DTU), Department of Civil Engineering, both as subcontractors.

Each group conducted their own independent experiments and wrote a report on their part of the project. Accordingly, this report is presented in two separate chapters: 1) Chapter 4 Research on Windows of Opportunity for Herder Use and 2) Chapter 5 Research on Environmental Fate and Effects of Chemical Herders.

A separate report entitled "*Research Summary: Herding Surfactants to Contract and Thicken Oil Spills for In-Situ Burning in Arctic Waters*" is also available and it reviews and documents the research that has been conducted on herding agents since 2003 (SL Ross and DCE 2014). The report was prepared by SLRoss and DCE – Danish Centre for Environment and Energy, AU.

Major Study Conclusions

- Window-of-opportunity testing
 - The thickness of slicks herded with OP-40 decreased slowly over the one hour tests (i.e., the slicks spread slowly). The thickness of slicks herded with Thick Slick 6535 declined less slowly, or not at all. One hour of effectiveness could be enough time for a complete herding and burning operation.
 - Evaporated crude oil is herded to greater thickness than fresh crude, providing the oil can still flow at the water temperature.
 - Herders contracted test oils with 20% emulsified water content (the maximum ignitable), but not with 50% water content.
 - Herders can still contract oil slicks at temperatures up to 8° - 10 °C below the oils' pour point. Wave action seems to help with this by keeping the slick in motion and fluid.
 - The presence of slush ice restricts both oil spreading and herder effectiveness. In 30% slush ice cover the herders can still function, but in 100% slush ice cover the oil does not spread and the herder is prevented from reaching the slick.
- Research on Fate and Effects of chemical herders
 - Small concentrations (in the range of 0.0-22.8 µg/L (parts per billion)) of herders were found in the water column samples taken at the end of the laboratory experiments.
 - Generally, after burning, the herder was mainly found on the water surface, though reduced in amount compared to pre burning.
 - Sub-lethal effects were seen after 48 hours of exposure at concentrations of herder (>12.5 mg/L) that was orders of magnitude higher than observed in laboratory burn experiments.
 - Thickslick 6535 biodegraded quickly (however, recovery of TS6536 was low) at cold temperatures. OP-40 had limited biodegradation over the 28 days testing.
 - Bioaccumulation testing indicated that Thickslick 6536 may not bioaccumulate while OP-40 has bioaccumulation potential.
- Impacts of Herders on Feathers from Arctic Sea Birds

- Monolayers of OP-40 and TS6535 did not cause feathers to sink, however, they did absorb more water than the controls. Herders spread very rapidly to monolayers in the open sea.
- The feathers exposed to surface loadings used to apply herders (150 $\mu\text{L}/\text{m}^2$ and 20 $\mu\text{L}/\text{m}^2$) of OP-40 sank within a few seconds after exposure. The feathers exposed to 150 $\mu\text{L}/\text{m}^2$, 20 $\mu\text{L}/\text{m}^2$ TS6535 did not sink, but slowly absorbed water. Note that these loadings are assumed to be transient in a real incident, and this limits the potential for birds to encounter them.
- Smoke Plume Analysis
 - The use of both herders did not have a negative impact on the primary BTEX compounds detected in the smoke plumes.
 - No significant increase in the products of combustion was detected in the smoke from in situ burning experiments using herded oil slicks.

Research on Windows of Opportunity for Herder Use

The goal of these experiments was to determine the window-of-opportunity for the two commercially-available herders (ThickSlick 6535 and OP 40) to contract slicks of weathered oils to ignitable thicknesses. The experiments involved a range of crude oils that were quantitatively evaporated and emulsified. Small and medium-scale herding experiments were carried out in the SL Ross laboratory and larger-scale tests were carried out at the CRREL facility in Hanover, NH to determine at what point (defined by evaporation and emulsion water content) the herders could no longer herd the slicks to an ignitable thickness in cold ice-free water and slush ice.

The herding effectiveness experiments were conducted in four experimental set-ups at the SL Ross lab and one at CRREL:

- 1 m^2 metal pans lined with a rinsed clean plastic film;
- A 10- m^2 pool created on the floor of the lab using lumber and plastic film;
- A rocking shaker used to simulate wave action;
- An 11 m x 1.1 m x 1.1 m refrigerated wind/wave tank with a computer-controlled wave generator and a fume hood suspended over the tank for ISB studies; and,
- Two experimental 5.3 m x 5.3 m x 15 cm test pools in the refrigerated Research Area at CRREL where the air temperature was maintained at -4°C .

The Windows-of-Opportunity test variables included:

- Two herding agents (ThickSlick 6535 and OP-40)
- Four crude oil types (Alaska North Slope, Endicott, Grane and Terra Nova);
- Three extents of evaporation for each crude (fresh and two degrees of evaporation);
- Two emulsion water contents for each degree of evaporation that was capable of forming at least meso-stable emulsions; and,
- Slush ice in selected tests.

The following conclusions were drawn from the Window-of-Opportunity test results:

- In general the OP-40 was slightly more effective with all four fresh crudes than the TS6535.
- The initial herded thickness achieved is a function of both herder and crude type.

- The thickness of slicks herded with OP-40 decreased slowly over the one hour tests (i.e., the slicks spread slowly). The thickness of slicks herded with TS6535 declined less slowly, or not at all.
- Evaporated crude oil is herded to greater thickness than fresh crude, providing the oil can still flow at the water temperature.
- Herders can contract slicks with 20% emulsified water content (the maximum ignitable), but not slicks with 50% water content.
- Herders can still contract oil slicks at temperatures up to 8° - 10 °C below the oils' pour point. Wave action seems to help with this by keeping the slick in motion and fluid.
- The presence of slush ice restricts both oil spreading and herder effectiveness. In 30% slush ice cover the herders can still function, but in 100% slush ice cover the oil does not spread and the herder is prevented from reaching the slick. In general, the OP-40 herder worked more effectively than the TS6535 in slush ice.
- The simulated wave action in the Dynamic Film Performance apparatus generally reduced herder effectiveness with the low Pour Point ANS crude compared to calm conditions, but increased herder effectiveness with the high Pour Point Terra Nova crude.
- During test burns, the ignited slicks restrained by herders would spread slightly during burning, then contract again as the flames extinguished. The burn efficiencies were slightly lower than burns of similar diameter and thickness in a metal containment ring. The burns of slicks restrained with OP-40 resulted in slightly higher removal efficiencies than those restrained by TS6535. The ANS crude had higher burn efficiencies than the Grane crude.
- Herded slicks in gentle waves in a wave tank tended to break up into smaller and smaller slicklets as wave period decreased. Once breaking waves were generated, the herder monolayer was quickly disrupted and the slicks spread and sheened.

Research on Fate and Effects of chemical herders

The goal of these experiments was to increase the knowledge about the environmental fate and effects of the two herders in the polar marine environment. Knowledge regarding the environmental impacts is crucial in order to carry out a well-founded Net Environmental Benefit Analyses (NEBA) prior to advising decisions-makers if and when herders can be allowed as the collecting agent in an ISB operational response situation.

The experiments involved two different crude oils both fresh and emulsified. Small-scale herding and burning experiments were carried out in the laboratories of DTU (Technical University of Denmark) for investigation of the physical fate of the herders during burning. The samples from the experiments were analysed for the herder content at the laboratories of DCE (Danish Centre for Environment and Energy, Aarhus University).

Environmental effects studies included toxicity testing and bioaccumulation of the two herders on high Arctic copepods (*Calanus hyberboreus*), the potential biodegradation in Arctic conditions and the impacts on Arctic seabirds (Thick-Billed Murre and Common Eider). All the species were collected in Greenland and part of the experiments were also conducted in Disko Bay, Greenland and completed in the laboratories of DCE.

A number of test burns at the SL Ross lab were sampled to determine if herder combustion products could be found in the smoke plume.

Burning experiments at DTU

Laboratory experiments were carried out in the Crude Oil Flammability Apparatus (COFA) in laboratories at DTU in order to study the thickening effect of the two herding agents and to generate samples for the toxicity, biodegradation and feather impact studies. The herders were applied around slicks of two fresh crude oils, Alaska North Slope (ANS) and Grane, and their corresponding emulsions with 25% water content. Moreover, the ignition, burning mechanisms and related parameters were studied. In addition to the main experiments, where the oil slicks were herded (post-herding application) followed by ignition, three series of different experiments were carried out. First, the herding capability was analysed for application of the herder prior to the oil application (pre-herding application). Here, the aim was to study the herding efficiency for a case that can simulate scenarios in the field where oil spills can occur due to a broken pipeline, or for scenarios where the herder could be used to block the oil spill from vulnerable areas such as shorelines, ports, aquifer and other protected marine areas. Second, the duration of the herding ability was studied (long-term) when the herder was post-applied. The objective for this procedure was to study the herding ability over a long term, because few studies have been reported in the literature for the such a case. Finally, the last series were control experiments where the oil was confined by a Pyrex Glass Cylinder upon ignition (i.e. there was no use of herder).

The following conclusions were made from these burning experiments:

- In general, ANS and Grane crude oils achieved burning efficiencies of, respectively, 37% and 21-26% in the current set-up. It is well known that the burning efficiency is a function of the experimental set-up and the experimental conditions, and these burning efficiencies fall in line with other experimental results from studies with similar, low, oil amounts. The fact that the burning efficiency was slightly lower in the current experiments can be explained by the fact that it was ensured that there was no re-radiation from the rig or from surrounding objects, and that forced convection (low exhaust velocity) was avoided. Also, the oil to water ratio was very small, so the water temperature was not changed during the experiments. Furthermore, based on current data and large-scale data from other studies, there is a clear correlation between the size of the pool (the amount of oil) and the burning efficiency. For smaller oil amounts, lower burning efficiencies are achieved, whereas the highest burning efficiencies (>90%) are achieved for large amounts of oil (field scale). As such, the current results can be scaled to show that the expected burning efficiency in the field would be above 90%.
- The ANS and Grane 25% water-in-oil emulsions resulted in much higher burning efficiencies than those for fresh crude oils, even though similar thickness were achieved, due to more intense boilover during the burning of the emulsified oil slicks. This boilover is an artefact of laboratory testing and is not normally observed in real burns at sea.
- OP40 outperformed TS6535 for most of the small laboratory experiments, which is as expected, because the former causes a greater reduction in the surface tension of the water.
 - In particular, TS6535 did not achieve as thick slicks as OP40, especially for Grane, and 3 mm thickness was not achieved as in other studies.
- The greatest slick thicknesses were achieved when the water was pre-treated with the herding agents. This is presumably due to an increased contact surface for the crude oil with the monolayer as the oil was never allowed to spread out. Then TS6535 was indeed able to thicken both crude oils with slick thickness above 3 mm.

- In the long-term laboratory experiments, the monolayer produced by OP40 seemed to lose its surface tension properties after 60 minutes, after which point the effect of the herder declined and after 6-8 hours the oil slick thickness returned to initial conditions. ThickSlick 6535, on the other hand, could keep ANS and Grane oil slicks herded for up to 100 and 350 hours, respectively. Considering that the full herding and burning process normally will be completed in less than 60 minutes, OP40 could still perform as needed

Physical Fate of Herder during Burning

The purpose of this part of the research project was to investigate the physical fate of the herder during burning. In the attempt to determine the physical fate, analyses of the herder were conducted after test burns in the Crude Oil Flammability Apparatus, i.e. fraction of herder remaining in the aquatic environment (water column and on the surface). Knowledge about the fate of the herder is important input to be able to perform a full NEBA including the use of herders together with ISB. This proved more difficult than anticipated when using standard tools and measurement techniques normally used in risk assessments. One issue was related to the strong surface active preferences of the herders, which result in very different physical and chemical behaviour compared to other chemicals that are normally evaluated for risk in the marine environment.

The following conclusions were drawn from these herder fate experiments:

- Small concentrations (in the range of 0.0-22.8 µg/L) of herders were found in the water column samples taken at the end of the laboratory experiments.
- For the post burn samples, water surface and water column, the concentrations are higher when the test oil is emulsified compared to fresh crude oil. This was noted for both oil types.
- Samples taken directly under the oil slick had overall higher concentration, in particular for OP-40.
- Generally, after burning, the herder was mainly found on the water surface, though reduced in amount compared to pre burning.
- The herders were able to re-thicken the oil after burn extinction.
- The decaying effectiveness of the herders with time is ascribed to be a combination of different processes: evaporation, dissolution/entrainment into the edge of the oil slick and a minor dissolution/dispersion into the water.

Toxicity and Bioaccumulation of Herders in High Arctic Copepod and Biodegradation of Herders in Arctic Surface Waters

The purpose of this work was to study the toxicity and bioaccumulation of the herders with the high Arctic copepod (*Calanus hyperboreus*), as well as to study the biodegradation of the herders in Arctic waters at low temperature. No standard Arctic test organisms exist. However, *Calanus hyperboreus* has been chosen as it is the key species in the Arctic regions because of its abundance and essential role in the Arctic food web and is therefore representative as a test organism for studying effect of chemicals in the Arctic environment. The copepod has been used previously in similar studies with success (Hjorth and Nielsen 2011; Nørregaard et al. 2014; Nørregaard et al. 2015)

No standards exist for toxicity testing with Arctic organisms. To cope with these challenges a science-based approach was followed in the design of the experimental set-up for the toxicity tests. It should be kept in mind that the experiments have been conducted in a well-equipped

but simple on-site field laboratory. It was decided to do the experiments in the field to secure sufficient high fitness of the organisms, as the long transportation from Greenland to Denmark was expected to stress the organisms unnecessarily.

The biodegradation experiments were conducted according to the OECD 309 Guideline for testing of chemicals - Aerobic Mineralisation in Surface Water – Simulation Biodegradation Test (OECD 309). This guideline is designed in such a way that makes it possible to also investigate biodegradation at Arctic conditions and with Arctic organisms.

In the guideline (OECD 309) it is written in Paragraph 23 that: "If unavoidable, stock solutions of non-volatile substances with poor water-solubility should be prepared by use of a volatile organic solvent, but the amount of solvent added to the test system should not exceed 1% v/v and should not have adverse effects on the microbial activity. The solvent should not affect the stability of the test substance in water". Since the chemical herders have a strong preference for a surface or interface rather than going into solution, acetone was used to prepare stock solutions to ensure that the herders were homogeneously dissolved in the water. The concentrations of acetone used are well below the limits reported for effects seen from acetone in different test standards (ECETOC 1996) and thus acetone is not expected to impact on the results. Without the use of stock solutions of herders in acetone, the herders will not go into the water phase and the test results will be misleading and would have indicated that the herders cannot be biodegraded and that the herder is not toxic because it never was in contact with the copepods.

The use of acetone was thus to ensure proper dosing of the herders to the test bottles for biodegradation, toxicity and bioaccumulation tests. The use of acetone was according to the OECD standards for testing poor water-solubility substances as described in the section above. However, it should be pointed out that the concentrations of herder in the water column during a real incident are expected to be several orders of magnitude lower than the sub-lethal effects concentrations found during toxicity testing.

The following observations were made based on the investigations of the inherent properties of the herders in relation to biodegradability, bio-accumulation and toxicity in Arctic conditions and with Arctic organism meeting the OECD guideline in relation to also duration of test periods:

Effects of dissolved herders on the behaviour and mortality of *Calanus hyperboreus* was observed over a period of 25 days. A distinct mortality was seen at the highest test concentrations of the herders. After 1 day 100% mortality was seen at 600 mg/L TS653. Markedly sub-lethal effect (very slow moving animals) was seen after 48 hours exposure in concentrations of 12.5 mg/L and 60 mg/L TS6535. More than 90% mortality was subsequent seen after 25 days at 60 mg/L TS6535. Corresponding, 100% mortality was seen at 12.5 and 60 mg/L OP-40 and sub-lethal effect after 48 hours exposure in concentrations of 2.5 mg/L OP-40. More than 90% mortality was subsequent seen after 25 days at 2.5 mg/L OP-40. All of these concentrations of herder in water are several orders of magnitude greater than the herder concentrations measured underneath the test slicks in the Crude Oil Flammability Apparatus. Further, exposing organisms to herders for 48 hours to 25 days is far longer than they would be exposed after a real incident.

- The results showed that the degradation of OP-40 was insignificant or low over 28 days in Arctic seawater. TS6535 disappeared quickly in the test bottles probably due to rapid biodegradation. However recovery rates for TS6535 in the chemical analysis was low.
- The results indicate that OP-40 may bioaccumulate and TS6535 may not bioaccumulate in the high Arctic copepods.

- It should be noted that recovery rates are low and particularly for TS6535 was difficult to measure and that some uncertainty must be attached to the results. The low recovery can be attributed to the poor solubility of the herders in water and that herders have a great tendency to be caught in the surface film, as well as degrade fast (TS6535). However, it must be noted that the studies on herders are complicated by the poor solubility and derived poor distribution of herders in water.

Impacts of Herders on Feathers from Arctic Sea Birds

The laboratory experiments included exposure tests of seabird feathers in sheens of herders followed by microscopic measurements of the feather microstructure, and changes in weight as a result of absorption of water, herders and/or oil. The exposure experiments were conducted in the laboratories of DCE – Danish Centre for Environment and Energy. The samples for testing were:

- Fresh samples of: herder (TS6535 and OP-40), oil (ANS) and a mixture of herder and oil
- Post burn samples i.e. surface fraction of oil (ANS) residue/herder mixture from burning experiments herded with OP-40 and TS6535 respectively. For details regarding the preparation of the burn residues see description in 5.2.
- Controls: seawater, solvent (Dichloromethane = DCM)

The following was concluded from these tests:

- For most of the exposure experiments the barbule Amalgamation Index decreased by decreasing the concentrations.
- No Observed Effect Concentration (NOEC) and the related No Observed Effect Slick Thickness (NOEST) were calculated. Thick-billed Murre feathers seem less sensitive than Common Eider feathers in the combined experiments with both crude oil and OP-40 results in the lowest effect thicknesses.
- Both herders significantly increase the feather weight and Amalgamation Index (AI).
- The dosages of herders on water included 150 $\mu\text{L}/\text{m}^2$, 20 $\mu\text{L}/\text{m}^2$ and 1-3 $\mu\text{L}/\text{m}^2$. The 150 $\mu\text{L}/\text{m}^2$ dosage is the recommended Application dosage applied to contract the oil in the field. This dosage will result in a monolayer of herder being fed, as it spreads out, from droplets of surplus herder, until the herder has spread out to a monolayer. The 20 $\mu\text{L}/\text{m}^2$ is the minimum effective dosage needed to contract the oil to maximum thicknesses, determined from laboratory experiments. This dosage will also result in a monolayer and droplets of surplus herder, until the herder has spread out completely. The 1-3 $\mu\text{L}/\text{m}^2$ is the estimated dosage that is expected to result in a monolayer without the droplets of surplus of herders. It is assumed that herders spread very rapidly to monolayers in the open sea, covering areas larger than the 20-150 $\mu\text{L}/\text{m}^2$ potential initial dosages.
- Monolayers of OP-40 and TS6535 did not cause feathers to sink, however, they did absorb more water than the controls.
- The feathers exposed to 150 $\mu\text{L}/\text{m}^2$ and 20 $\mu\text{L}/\text{m}^2$ of OP-40 sank within a few seconds after exposure.
- The feathers exposed to 150 $\mu\text{L}/\text{m}^2$ and 20 $\mu\text{L}/\text{m}^2$ TS6535 did not sink, but slowly absorbed water.

Smoke Plume Analysis

The SL Ross experiments included multiple burns with oil slicks contained by mechanical methods and by chemical herders so that comparisons could be made. The smoke plume of several burns

were sampled and sent for analysis at Environment Canada to determine if the herder could be detected in the plume, or if there were any significant changes in the composition of the plume. Two parent oils, Alaska North Slope pipeline crude and Grane crude from a platform off Norway were used in the experiments. Two herders, ThickSlick 6535 and OP-40 were used.

The following was concluded from these tests

- The use of both herders did not have a negative impact on the primary BTEX compounds detected in the smoke plumes.
- The chromatograms did not show obvious signs of herder
- No significant increase in the products of combustion was detected in the smoke from in situ burning experiments using herded oil slicks.

Recommendations

Several recommendations arose from the study:

- Care must be taken in the production and storage of TS6536. The batch of TS6535 provided to CRREL was not as effective as the others (SL Ross and DCE) and was either not properly formulated or mixed. After being warmed and shaken before each test, the performance of this batch of TS6535 seemed to improve.
- Additional large-scale field testing in actual drift ice conditions and open water with both herders is required to fully define their Window of Opportunity.
- Further studies are needed to more deeply examine the findings in the report for the herder fate , to attempt to distinguish the individual fate processes and their relative importance in the resulting fate of the herder.
- Biodegradation tests of TS6535 should be done that focus on the first hours and days, to determine the degradation rate.
- The long term effects from herders on seabirds should be studied, to see if the impacts from the herders on the microstructure is long-lived or if the birds are able to preen or otherwise remove the herder.

1. INTRODUCTION

Herding agents were initially developed in the 1970's as a method of contracting and hence thickening oil slicks prior to mechanical recovery. However, it was discovered during field tests that herded slicks began to spread again within tens of minutes of treatment in all but relatively calm seas. Therefore, herders were never applied during an actual offshore spill because mechanical recovery requires longer periods to implement.

Previous research:

A research programme initiated in 2003 by SL Ross Environmental Research Ltd to advance oil spill response in ice found that the contracting ability of herding agents persisted long enough to enable in-situ burning (ISB) of relatively fresh, fluid oils in broken or drift ice. This multi-year, multi-partner programme involved:

- A small scale (1 m²) preliminary assessment of a shoreline-cleaning agent with oil herding properties was carried out in 2003 to assess its ability to herd different oils on cold water and among ice (SL Ross 2004).
- Small-scale (1 m²) experiments were carried out next in 2005 to explore the relative effectiveness of three oil hydrocarbon-based herding agents in simulated ice conditions; followed by larger scale (10 m²) quiescent pan experiments to explore scaling effects; small-scale (2 to 6 m²) wind/wave tank tests to investigate wind and wave effects on herding efficiency; and finally, small ignition and burn tests (SL Ross 2005). These tests identified ThickSlick 6535 as an effective herding agent on cold water and in ice conditions.
- Experiments were done with the ThickSlick 6535 herder at the scale of 100 m² in the indoor Ice Engineering Research Facility Test Basin at the US Army Cold Regions Research and Engineering Laboratory (CRREL) in November 2005 (SL Ross 2007).
- Experiments were undertaken with the ThickSlick 6535 herder at the scale of 1000 m² at Ohmsett¹ in artificial pack ice in February 2006 (SL Ross 2007).
- A series of 20 burn experiments were carried out in 2007 with the ThickSlick 6535 herder at the scale of 30 m² in a specially prepared test basin containing broken sea ice in November 2006 at the Fire Training Grounds in Prudhoe Bay, AK with fresh crude oil (SL Ross 2007).
- Field tests in pack ice in the Barents Sea were done in 2008 (Buist et al. 2010b). One experiment involved the release of 630 L of fresh Heidrun crude in a large lead. The free-drifting oil was allowed to spread for 15 minutes until it was far too thin to ignite (0.4 mm), and then ThickSlick 6535 herder was applied around the slick periphery. The slick contracted and thickened for approximately 10 minutes at which time the upwind end was ignited using a gelled gasoline igniter. A 9-minute long burn ensued that consumed an estimated 90% of the oil.
- Studies on better herding surfactants were completed between 2008 and 2010, and identified that the OP-40 silicone-based herder was identified as being more efficient at herding than the ThickSlick 6535. (Buist et al. 2010a)

¹ Ohmsett is the National Oil Spill Response Test Facility, located in Leonardo, New Jersey, USA. The name Ohmsett is an acronym for "Oil and Hazardous Materials Simulated Environmental Test Tank"

- Work on developing techniques for applying herding agents to slicks in ice-affected water commenced in 2010 (Buist and Before 2011).

As a result of the success with herders for use together with ISB in ice, a two-year programme of R&D in the SL Ross lab and at Ohmsett was undertaken in 2009 to determine if there was a potential to use herding agents to improve other areas of marine oil spill response (Buist *et al* 2010c), specifically :

- Employing herding agents in drift ice to enhance recovery of spilled oil with skimmers;
- Using herders to clear oil from marsh areas; and,
- Applying chemical herders around oil slicks on the open ocean to improve the Application effectiveness of subsequent dispersant application

In 2011 a research programme was carried out to explore the use of herding agents for ISB in open water conditions as a rapid-response technique for oil spills offshore. The research was conducted in two parts: the first involved laboratory testing to identify the most effective herding agent(s) for warmer water conditions; the second involved experiments at Ohmsett to quantify the persistence of the herder monolayer in waves. The results showed that the monolayer of each of the two most effective herders will survive for more than 45 minutes in a calm sea. The presence of breaking or cresting waves rapidly disrupts the herder monolayer and the oil slick resulting in the production of many small slicklets from the herded oil slick and the re-spreading of the oil to response inefficient thin slicks. The monolayer survives for considerable periods of time in a swell condition, but the constant stretching and contracting of the herded slick results in elongating the oil slick and slowly breaking it into smaller segments (SL Ross 2012), although this may not occur for oil slicks with dimensions much greater than the wavelength.

An application system, consisting of a pump, controls and reservoir has been designed by DESMI-AFTI to be placed inside an appropriate helicopter. It incorporates a reel-able hose that is used to lower the application nozzle to the correct height above the water for herder application. Dry land, static trials were conducted in September 2013 and helicopter flight trials were conducted in October 2014 and March 2015 (Potter *et al.* 2015). A back-pack sprayer system for herder application from a small vessel is available off-the-shelf, with only minor modifications required for cold-temperature use.

Herders in use:

Desmi-AFTI worked in conjunction with S.L. Ross Environmental Research to get approval to use herders in North American waters. The proscribed test data (physical properties, behaviour on water and toxicity) from an accredited laboratory on three candidate herding agents (also called surface collecting agents) was submitted to the U.S. EPA for approval to list them on the National Contingency Plan (NCP) Product Schedule. Two herders were listed and are now commercially available. These two (ThickSlick 6535 and OP-40) can be used, with the Federal On-scene Commander's (FOSC's) concurrence, for spill response operations in U.S. waters. OP-60 did not pass the mixing test proscribed by the USEPA and was not listed.

ThickSlick 6535 is a blend of 65 volume % sodium monolaurate (Span 20), the surfactant, and 35% 2-ethyl butanol solvent. The active ingredient of ThickSlick 6535 is used as a food additive, in household cleaners as well as in cosmetics, fine fragrances and other toiletries. OP-40 is a proprietary polydimethylsiloxane copolymer compound. Surfactants of the type used in OP-40 are used in household and automotive care products as well as in hair conditioners and skin care products. Quantities (200 L) of the two herders listed on the NCP Product Schedule have been

produced and are stockpiled at DESMI-AFTI in Buffalo. Samples of three herders (ThickSlick 6535, OP-40 and OP-60) have been sent to Environment Canada, along with all the EPA test data, for their consideration for use in Canadian oil spill responses.

Environmental assessment of herders:

Although some EPA test data on the potential effects of herders on the environment are available from the approval process noted above, knowledge about the chemicals' effects and bioaccumulation on Arctic organisms that live near or are associated with sea ice does not exist. The evaluation of herders for approval by the US EPA is based on data from standard laboratory tests which are performed with temperate or tropical species over a period of 1-4 days at temperatures between 15-20 °C . However, the environment and biology in Arctic waters are characterized by low temperatures in surface waters throughout the year, large seasonal variations in solar radiation, high prevalence of sea ice, a unique animal and plant life adapted to the cold climate and life associated to the sea ice, general slow biological processes, short food chains and a high content of lipids (fats) in the organisms (AMAP, 1998). The relative high content of lipids / fats serves partly as an energy reserve to withstand long periods without food and partly as insulation against the cold environment. To reduce the uncertainty from the temperate standard tests with potential irrelevant species and test temperatures for Arctic conditions, toxicity and bioaccumulation of herders was investigated in laboratory tests with high Arctic copepods at Arctic temperatures. Copepods occupy a key function in high Arctic seas as food for fish, seabirds and marine mammals.

No herders have been approved for use in other nations' Arctic waters, thus the data and results from this project can serve as a basis for performing a robust windows-of-opportunity and environmental risk evaluation of herders for ISB in Arctic seas.

2. OBJECTIVE

The objective of this multi-project and interdisciplinary research programme was to advance the knowledge of chemical herder environmental fate, effects and performance in order to expand the operational utility and environmental assessment of ISB in open water and in ice-affected waters with drift ice conditions.

3. REPORT LAYOUT

This project was undertaken by two main research groups:

- SL Ross Environmental Research Ltd as prime contractor carried out the research on the windows of opportunity for herder use at their laboratory in Ottawa, Canada and at CRREL in New Hampshire, U.S.A.
- DCE - Danish Centre for Environment and Energy, at Aarhus University in Denmark performed the herder effects research in co-operation with the Technical University of Denmark (DTU), Department of Civil Engineering, both as subcontractors.

Each group conducted their own independent experiments and wrote a report on their part of the project. Accordingly, this report is presented in two separate chapters: 1) Chapter 4 Research on Windows of Opportunity for Herder Use and 2) Chapter 5 Research on Environmental Fate and Effects of Chemical Herders.

A separate report entitled "*Research Summary: Herding Surfactants to Contract and Thicken Oil Spills for In-Situ Burning in Arctic Waters*" is also available and reviews and documents the research that has been conducted on herding agents since 2003 (SL Ross and DCE 2014). <http://www.arcticresponsetechnology.org/wp-content/uploads/2015/05/Herder-Research-Summary.pdf>

4. RESEARCH ON WINDOWS OF OPPORTUNITY FOR HERDER USE

4.1 Goal

The goal of these experiments was to determine the window of opportunity for two commercially-available herders (ThickSlick 6535 and OP 40) to contract slicks of weathered oils to ignitable thicknesses. The experiments involved a range of crude oils that had been quantitatively evaporated and emulsified. Small and medium-scale herding experiments were carried out in the SL Ross laboratory in Ottawa, ON and larger-scale tests were carried out at the US Army Corps of Engineers Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, NH to determine at what point (defined by evaporation and emulsion water content) the herders could no longer herd the slicks to an ignitable thickness in cold ice-free water and slush ice.

4.2 Small-scale Experiments at SL Ross

The herding experiments were conducted in four experimental set-ups at the SL Ross lab:

- 1 m² metal pans lined with a rinsed clean plastic film (Figure 1);
- A 10- m² pool created on the floor of the lab using lumber and plastic film (Figure 2);
- A rocking shaker used to simulate wave action (Figure 3); and,
- An 11 m x 1.1 m x 1.1 m refrigerated wind/wave tank with a computer-controlled wave generator and a fume hood suspended over the tank for ISB studies (Figures 4, 5 and 6).



Figure 1: Lined 1-m² steel pans used for experiments.



Figure 2: Lined 10-m² pool.



Figure 3: Rocking shaker for DFP tests.



Figure 4: Herded slick in SL Ross wind/wave tank.

4.2.1 Methods

The crude oils for the experiments were artificially evaporated by sparging compressed air into pre-weighed 20-L cans of the oils. The cans were weighed periodically to measure progress. As the mass loss slowed, electric band heaters were attached to the outside of the cans to accelerate the evaporation. The target evaporative losses were based on earlier spill-related property studies of the four crudes.

4.2.1.1 1-m² Pan Experiments

The 1-m² pan test matrix included:

- Two herding agents (ThickSlick 6535 and OP-40)
- Four crude oil types (Alaska North Slope, Endicott, Grane and Terra Nova);
- Three extents of evaporation for each crude (fresh and two degrees of evaporation);



Figure 5: New aluminium wind wave tank in SL Ross laboratory.



Figure 6: Herded slick burning under fume hood suspended over wind/wave tank.

- Two emulsion water contents for each degree of evaporation that was capable of forming at least meso-stable emulsions; and,
- Slush ice in selected tests.

The 1-m² pan tests were all done with cold (approximately 0°C), 35 % salt water. Additional experiments were done as randomly-selected duplicates. The general procedure for a 1-m² pan experiment was:

1. Place 20 L (a depth of 2 cm) of cold salt water in each 1-m² pan (Figure 1) lined with freshly rinsed (with tap water) new plastic film. For some oils with high Pour Points, warmer water was used.

2. Take a sample of the water from the surface using a Petri dish and measure the water-air interfacial tension (IFT) using the DuNuoy Ring Tensiometer. If the IFT reading was less than 60, the water and film was replaced.
3. Add a bag of crushed ice cubes (simulating slush ice) to pan, if required.
4. Ensure that the furnace, all fans and open doors are closed so they cannot create a draft over the pans.
5. Carefully pour 500 mL of the crude on the water using a plastic paint scraper as a spill plate; making sure that it does not stick to the bottom of the pan while being poured.
6. Place a sign on the pan that will be visible in the photos denoting test number, conditions and photo time (0, 1 min, 10 min, etc.)
7. Allow the oil to spread to equilibrium and take a digital photograph from overhead for subsequent oil area analysis.
8. Apply prescribed amount (150 μ L) of herding agent to open water area with micropipette.
9. Allow the oil to contract and take another digital photograph after one minute, 10 minutes, 30 minutes and 1 hour.

The slicks (including any oil sheen) in the photographs were corrected for perspective, converted into black and white images using Paint Shop Pro (Figure 7) and then a computer program (Image J) was used to count the number of black pixels. The area of the slick in the photograph is then calculated by dividing the total number of black pixels by the number of pixels per square centimetre in the original image. The average slick thickness is estimated by dividing the volume of oil added originally by the calculated area. The error in estimating area should be quite small, less than 5% taking into account parallax errors at the sides of the pans. Errors in the average slick thickness would increase as time progressed, as evaporation losses are not taken into account, but in the quiescent lab environment over the period of an hour would not likely exceed 10% (SL Ross 2004 and 2005).

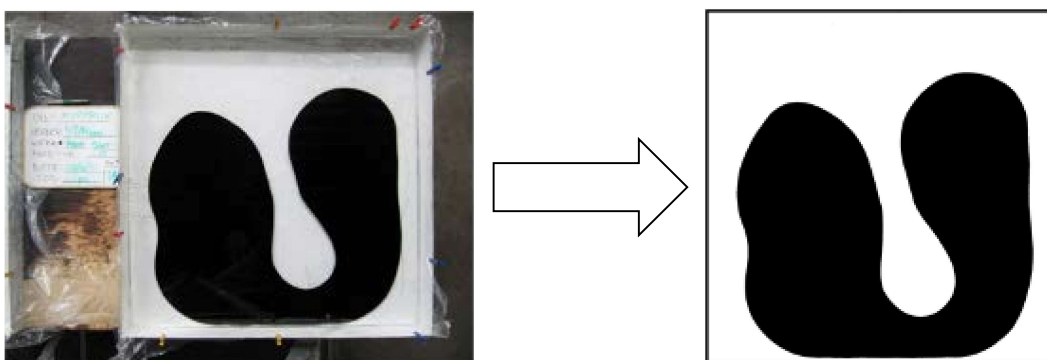


Figure 7: Determining slick area using overhead digital photos.

4.2.1.2 *Dynamic Film Performance Experiments*

The Dynamic Film Performance (DFP or Rocking Shaker – see Figure 3) test matrix included:

- Two herding agents (ThickSlick 6535 and OP-40)
- Three crude oil types (Alaska North Slope, Grane and Terra Nova – Endicott was excluded due to its very high pour point);
- Three extents of evaporation for each crude (fresh and two degrees of evaporation); and,

- Two emulsion water contents for each degree of evaporation that was capable of forming at least meso-stable emulsions.

The DFP experiments were done with 0°C, 35 ‰ salt water in a small environmental chamber, to maintain the water temperature near freezing during the 1-hour procedure. Additional experiments were done as randomly-selected duplicates.

The general procedure for a rocking shaker tray experiment was:

1. Place 1.115 L of 0°C water (\approx 2 cm deep) in each of two trays (18 cm wide x 28 cm long).
2. Take a sample of the water from the surface using a Petri dish and measure the water-air interfacial tension (IFT) using the DuNuoy Ring Tensiometer. If the IFT reading is less than 60, replace the water and retry.
3. Carefully place 50 mL of the test oil on the water using a spill plate, making sure that it does not stick to the bottom of the tray while being poured.
4. Place a sign beside each tray that will be visible in the photos denoting test number, conditions and photo time (0, 1 min, 10 min, etc.).
5. Allow the oil to spread to equilibrium and take a digital photograph from overhead for subsequent oil area analysis.
6. Apply approximately 10 μ L of herding agent to an open water area with a micropipette (the target dose for the herder is 7.5 μ L based on a recommended treatment of 150 μ L/m²; however, it is impossible to deliver an accurate dose with the viscous herder which tends to form discrete droplets at the end of the micropipette that will only detach at discrete volumes of approximately 5 μ L).
7. Allow the oil to contract and take another digital photograph after one minute.
8. Carefully place the trays on the rocking shaker and allow them to equilibrate to the test temperature in the environmental chamber, then start the shaker and timer. Rocking angle and frequency to be 10° at 0.25 Hz, representing a moderately steep swell in pack ice with a period of 4 seconds (SL Ross and DF Dickens 1987).
9. After 10 minutes and 30 minutes, stop the shaker, gently remove the trays re-photograph the slicks and replace the trays on the shaker.
10. Stop experiment after 1 hour, gently remove the trays re-photograph the slicks.
11. Remove tray, recover oil with sorbent pad, empty water from trays, clean with Alconox and hot water and rinse thoroughly with hot water.

4.2.1.3 10-m² Pool Tests

The oil and herder combinations tested at a scale of 10 m² were selected based on the results of the 1-m² and DFP experiments. ANS and Grane crude (fresh and evaporated) were selected. Some experiments involved slush ice and some involved emulsions.

The 10-m² experiment (Figure 2) was performed in a rectangular, plastic-lined wooden frame (3.05 m x 2.95 m x 9 cm deep) lined with a new, rinsed sheet of 1-mil plastic film to ensure a clean, uncontaminated surface. White plastic sheets were attached to the bottom of the frame to increase the contrast between oil and water in the photos.

The general procedure for a 10-m² pan experiment was:

1. Place 200 L (a depth of \approx 2 cm) of cold, 35 ‰ water in the 10-m² pool lined with freshly rinsed (with tap water) new plastic film.

2. Take a sample of the water from the surface using a Petri dish and measure the water-air interfacial tension (IFT) using the DuNuoy Ring Tensiometer. If the IFT reading is less than 60, replace the water and film and retry.
3. Place a sign at the edge of the pool that will be visible in the photos denoting test number, conditions and photo time (0, 1 min, 10 min, etc.).
4. Ensure that the furnace, all fans and open doors are closed so they cannot create a draft over the pans.
5. Carefully pour 1 L of the oil on the water, making sure that it doesn't stick to the bottom of the pool while being poured.
6. Allow the oil to spread to equilibrium and take a digital photograph from the rafters overhead for subsequent oil area analysis.
7. Apply the prescribed amount (1500 μ L) of herding agent to open water area around edge of pool with micropipette.
8. Allow the oil to contract and take another digital photograph after one minute, 10 minutes, 30 minutes and 1 hour.
9. Remove oil with sorbent pads, pump water from pool, remove plastic film, and replace film for next experiment.
10. Restart furnace, fans, etc.

4.2.1.4 *Wind/Wave Tank Experiments*

The oil and herder combinations tested in the SL Ross wind/wave tank were selected based on the results of the 1-m² DFP and 10-m² experiments. Fresh and evaporated ANS was used for the burn experiments and fresh Grane and ANS were used in the monolayer persistence experiments.

For the wind/wave tank experiments (Figures 4, 5 and 6), 4' x 8'- sheets of white signboard were laid on the bottom of the tank and weighted down in order to improve the discrimination between oil and water in the overhead photos and video. A test area was created by isolating an area of water surface with floating barriers stretched from one side of the tank to the other. This eased cleaning of the test area water surface between experiments. For the ISB experiments, metal heat shields were installed along the sides of the tank and the metal fume hood was swung over the burn area. The smoke from the burns was removed with a 200-m³/min fan, through a 60-cm metal duct that is connected to the fume hood suspended approximately 1 m above the water surface (Figure 8).



Figure 8: Wind/wave tank set up for burn experiments with heat shields and exhaust hood.

The general procedure for a wind/wave tank monolayer persistence experiment was:

1. Raise the floating barriers at either end of the test section and thoroughly clean the water surface with sorbent pads to remove any oil or herder traces.
2. Take a sample of the water from the surface using a Petri dish and measure the water-air interfacial tension (IFT) using the DuNuoy Ring Tensiometer. If the IFT reading is less than 60, clean the test area again.
3. Place a sign at the edge of the tank that will be visible in the video and overhead photos denoting test number, conditions and approximate test time of day.
4. Apply prescribed amount (500 μL) of herding agent to open water area with micropipette. Add additional herder as needed during the experiment to make up losses past the floating barriers.
5. Turn on the video.
6. Carefully pour 500 mL of the crude on the water; making sure that it doesn't submerge while being poured.
7. Allow the oil to spread to its herded equilibrium and record an image from overhead.
8. Turn on the wave generator to produce non-breaking waves and turn on/off the fan to counterbalance the wave drift.
9. At proscribed time intervals (to be determined after an initial dry run) increase the wave generator to produce steeper, more energetic waves. The wave program used involved generating 10-cm high waves with a 2-s period for 2 minutes, then reducing the period to 1.6 s for the next 2 minutes, 1.4 s for the next 2 minutes, 1.0 s for the penultimate 2 minute period and then finally reducing the period to 0.6 s. At this last setting, the 10-cm waves were breaking.
10. Stop wave generator, recover oil and herder with sorbent pads.

A typical ISB experiment in the wind/wave tank involved the following steps:

1. Insert barriers at either end of the heat shielded test section and thoroughly clean the water surface with sorbent pads to remove any oil or herder traces.
2. Take a sample of the water from the surface using a Petri dish and measure the water-air interfacial tension (IFT) using the DuNuoy Ring Tensiometer. If the IFT reading is less than 60, reclean the test area.
3. A volume of 400 mL (to form an approximately 40-cm diameter herded slick) of fresh crude oil is measured into a graduated cylinder and weighed.
4. Place a sign at the edge of the tank that will be visible in the video denoting test number, conditions and approximate test time of day.
5. For those experiments involving pre-treatment of the water surface of the tank, 500 μ L of the herder is placed on the water surface using a micropipette.
6. The oil is carefully poured onto the surface of the tank.
7. Ignition is attempted first with a propane soldering torch flame.
8. A stopwatch and video records the following times: initial ignition time, 50% flame coverage of slick; full ignition (100% flame coverage); time to the vigorous (or intense) burn phase; 50% flame extinction; and, extinction.
9. After extinction of the flame, pre-weighed rectangles of sorbent are used to recover the residue from the water surface. After use, each pad is shaken to remove as much water as possible. Then the pads were reweighed to determine the mass of residue. The sorbent pads are then hung up to dry overnight, and reweighed after any water had evaporated. It is assumed that very little of the burn residue evaporates in the same time period.

4.2.1.5 *Test Oils*

Four crude oils were selected for these tests:

- Alaska North Slope pipeline crude (sample obtained from a refinery in California in 2013)
- Endicott crude from one of the producing fields on the North Slope of Alaska (sample obtained from a flow station in 2004)
- Grane crude from a platform off Norway in 2014.
- Terra Nova crude from a transshipment tanker load taken from the production FPSO located 330 km of the coast of Newfoundland in 2002.

Table 1 summarizes the key physical properties of the fresh and evaporated crude oils.

4.2.1.6 *Test Herders*

Two herders, approved for listing on the U.S. National Contingency Plan Product Schedule, were selected for this programme:

- ThickSlick 6535; and,
- OP-40

Their properties, as submitted to the U.S. EPA for the listing, are given in Table 2.

Conceptual design for a long-range aerial ignition system for in situ burning

Table 1 Physical Properties of Test Crude Oils.

ANS Crude 2014		Endicott Crude 2004		Terra Nova Crude 2002		Grain Crude 2014 (properties from 2012 sample analyses by SINTEF)		
Evaporation (Volume %)	0	23.27	31.44	5.3	0	8.73	20.21	
Density (g/cm ³)	0.889	0.929	0.942	0.937	0.879	0.897	0.910	
0 °C	0.874	0.914	0.928	0.925	0.872	0.886	0.900	
20 °C				0.881	0.868	0.881	0.895	
Dynamic Viscosity (mPa.s)	at approx 180 s ⁻¹ except 31.4% evap 0°C at 120 s ⁻¹		Dynamic Viscosity (mPa.s) at 40 s ⁻¹		Dynamic Viscosity (mPa.s @ about 100 s ⁻¹)		Dynamic Viscosity (mPa.s) at 100 s ⁻¹	
0 °C	13	686	2,778	3095	1 °C	1492.0	8972.0	667
20 °C	13	91	224	342	10 °C	555.6	1396.0	1,275
Kinematic Viscosity (mm ² /s)	45	738	2,948	4159	15 °C	320.9	496.6	709
0 °C	15	99	242	370	10 °C	1664.2	8661.1	1,345
20 °C					15 °C	626.5	1550.6	
Interfacial Tension (dyne/cm)					15 °C	364.5	554.9	
Oil/Air	27.0	30.4	31.8	34.7	Interfacial Tension (dyne/cm)			
Oil/Seawater	15.9	17.7	19.6	39.0	Oil/Air	29.8	31.7	
					Oil/Seawater	27.4	28.6	
Pour Point (°C)	-18	-3	-3	15	Pour Point (°C)	18	21	
Flash Point (°C)	<-10	66	119	55	Flash Point (°C)	12	26	
Emulsion Formation-Tendency and Stability @	3.1 °C	Very Likely Emulsified	Very Likely Emulsified	0 °C	Emulsion Formation-Tendency and Stability @	10 °C	10 °C	
Tendency	39%	39%	36%	43%	Tendency Index	Very likely	Very likely	
Stability	17%	17%	17%	39%	Stability Index	Very stable	Very stable	
Water Content				0%	Water Content	64%	65%	
Emulsion Formation-Tendency and Stability @	18.6 °C	Very Likely Emulsified	Very Likely Emulsified	15 °C	Emulsion Formation-Tendency and Stability @	77%	85%	
Tendency	33%	33%	33%	13%	Tendency	Very stable	Very stable	
Stability	0%	0%	0%	23%	Stability	Very stable	Very stable	
Water Content				0%	Water Content	85%	85%	

Table 2 Summary of Test Results for U.S. EPA Approval for Listing on NCP Product Schedule

TEST		ThickSlick 6535	Siltech OP-40
	Units	Results	Results
NCP Category		Surface Collecting Agent	Surface Collecting Agent
Toxicity tests			
Herder			
M. bahia 48-hr LC50	ppm	286	6.83
M. beryllina 96-hr LC50	ppm	138	3.33
No.2 Fuel Oil			
M. bahia 48-hr LC50	ppm	2.43	6.43
M. beryllina 96-hr LC50	ppm	37.6	40.5
10:1 No.2 Fuel Oil / Herder			
M. bahia 48-hr LC50	ppm	1.53	3.27
M. beryllina 96-hr LC50	ppm	5.91	9.7
Reference Toxicant- Sodium Dodecyl Sulfate			
M. bahia 48-hr LC50	ppm	8.23	8.68
M. beryllina 96-hr LC50	ppm	3.02	2.33
Analytical tests			
Key Findings Summary			
Flash Point		>180 °F (82°C)	>180 °F (82°C)
Pour Point		21.2 °F (-1.7°C)	-74.2 °F (-59°C)
Viscosity	cSt (mm ²)	24.7	8.27
Viscosity @100°F	SUS [*]	118	53
Specific Gravity@60°F (15°C)		0.974	0.988
Surface Collecting Agent Test		PASS	PASS
Phase Separation		None	None
Freezes at		11.2°F (-24°C)	-95.8°F(-71°C) ((-71°C)
Solubility		Partial Miscibility	Partial Miscibility
pH		6.45	10.1

* Saybolt Universal Seconds

4.2.2 Results

4.2.2.1 1-m2 Pan Experiments

Figure 9 shows the results of the experiments with fresh and evaporated ANS crude on cold, salt water. The experiments with the OP-40 herder are shown in shades of red on the left of the chart, and those with ThickSlick 6535 (TS6535) are shown on the right of the chart in shades of blue. A duplicate experiment was performed with

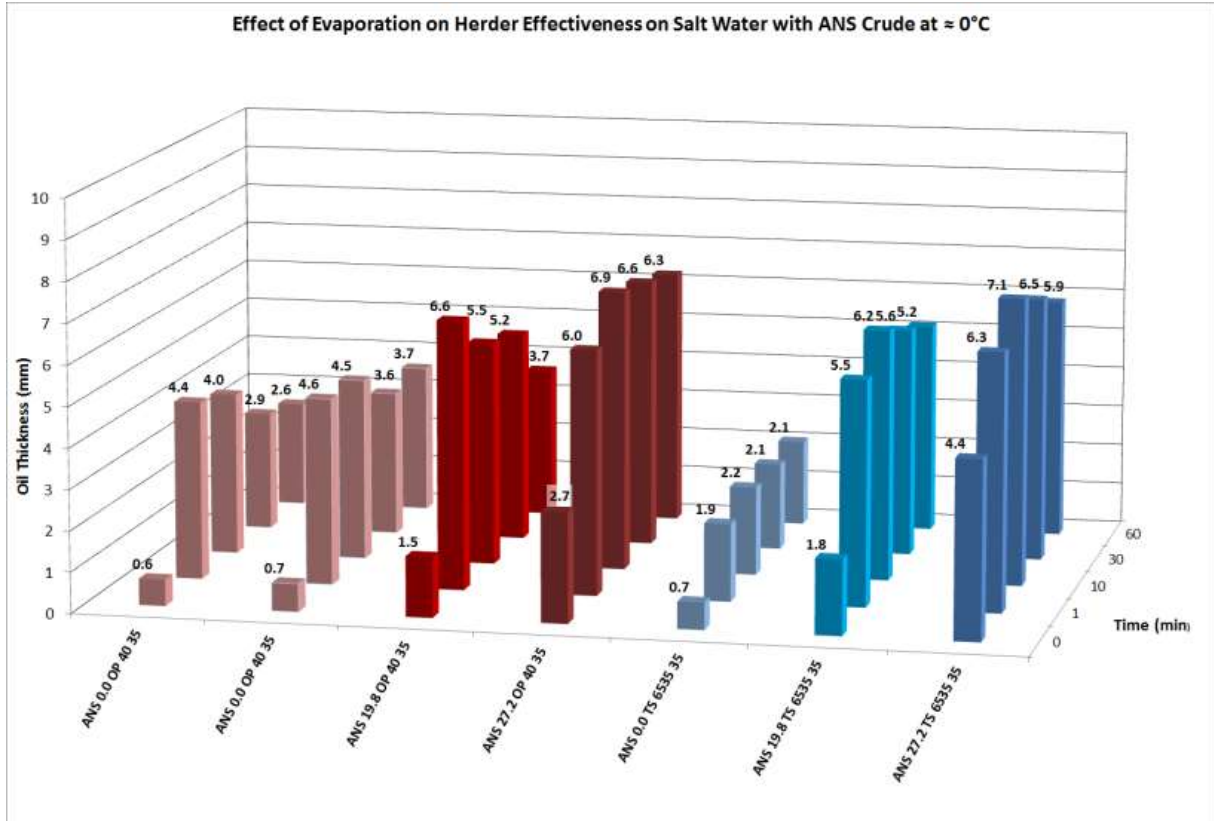
the OP-40 herder with fresh ANS crude. ANS crude would not form a sufficiently stable emulsion at the degrees of evaporation used in these experiments (SL Ross 2014). The nomenclature of the test identifiers on the x-axis is: XXX Y.Y ZZZZZ A.A

where: XXX \equiv Letter code for crude oil type
Y.Y \equiv Percent evaporated
ZZZZZ \equiv Letter/number designation of herder
A.A \equiv Salinity of water in pan in ppt

The initial spreading of the fresh ANS crude was quite typical of what has been observed in other experiments with this crude oil (e.g., SL Ross 2005 and SL Ross 2008) with equilibrium thicknesses of the crude of 0.6 to 0.7 mm in the 1-m² pan. The OP-40 herder was more effective than the TS 6535 herder with fresh ANS crude, achieving a herded thickness of 4.4 to 4.6 mm one minute after application. This thickness declined over the one-hour test period to 2.6 to 3.6 mm. In comparison, the TS6535 herder achieved a herded thickness of 2.9 mm that slowly declined to 2.1 mm after 60 minutes.

The 19.8% (by mass) evaporated ANS did not spread as much initially as the fresh crude: equilibrium thicknesses of 1.5 and 1.8 mm were attained before herder addition. The OP-40 performed slightly better than the TS6535 initially with the 19.8% evaporated ANS, but by the end of the experiments the TS6535 had maintained a 5.2 mm thickness while the OP-40 herded thickness had declined to 3.7 mm.

The 27.2 % evaporated ANS crude did not spread initially nearly as much as the 19.8% evaporated samples. The pour point of the 27.2% evaporated sample would have been near 3°C. The water temperature at the start of the OP-40 experiment was -0.3° and at the start of the experiment with TS6535 was -1°C. Even at water temperatures just below the oil's pour point, both herders contracted the slicks within one minute: OP-40 achieved a thickness of 6 mm and TS6535 achieved a thickness of 6.3 mm. The experiments were conducted in 10 to 15°C air temperatures, so over the one-hour time of the test, the water temperatures would have warmed slightly. Both herders maintained the initial thickness over the one-hour experiment.



X-axis: legend XXX Y.Y ZZZZZ A.A, where XXX ≡ Letter code crude oil type; Y.Y ≡ % evaporated; ZZZZZ ≡ herder; A.A ≡ Salinity of water in ppt

Figure 9: Results of 1-m² experiments with fresh and evaporated ANS crude

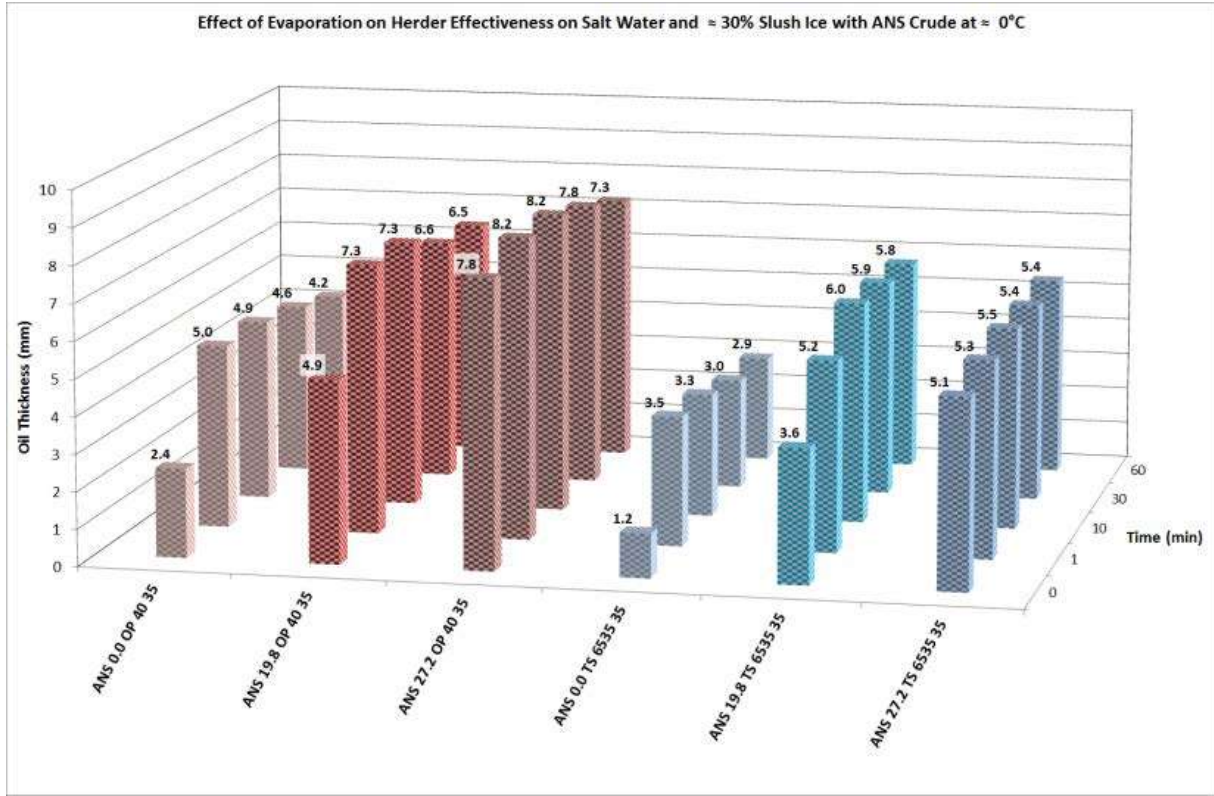
Figure 10 shows the results of herding experiments with the ANS crude in pans to which slush ice (simulated by adding a bag of crushed ice cubes to the water in the pan at the beginning of the experiment) has been added. It is clear that the presence of the slush ice restricts the initial spreading of the oil. For the experiments with the fresh crude the initial equilibrium slick thickness was 2.4 and 1.2 mm, compared to 0.6 to 0.7 mm in the absence of slush ice. For the experiments with the 19.8% evaporated ANS, the initial equilibrium thicknesses in slush ice were 3.5 and 4.9 mm compared to 1.8 and 1.5 mm in the ice-free experiments. For the 27.2% evaporated experiments, initial equilibrium thicknesses were 2.7 and 4.4 mm in the open water pans and 7.8 and 5.1 mm in the pans with slush ice.

The herders were effective on the fresh and 19.8% evaporated ANS crude in slush ice. The OP-40 herder was more effective on the fresh ANS crude than the TS6535, achieving an initial herded thickness of 5mm, compared to 3.5 mm for the TS6535. At the end of the tests the OP-40 had maintained a 4.2 mm thickness, while the TS6535 had maintained a 2.9 mm thickness. With the 19.8% evaporated ANS in slush ice, the OP-40 increased the oil thickness to 7.3 mm initially and 6.6 mm after an hour: the TS6535 increased the oil thickness to 5.2 mm initially and 5.4 mm after one hour. Neither herder had an appreciable effect on the 27.2% evaporated ANS in the slush ice conditions, likely due to its Pour Point being above ambient temperatures.

Figure 11 shows the data from the experiments with fresh and evaporated (1.4% and 6.2% mass loss) Endicott crude on 20°C salt water. The warm water experiments were necessary because the Pour Point of the fresh Endicott crude was 12°C. The Pour Point of both evaporated samples was 15°C (SL Ross 2008). The experiments with the OP-40 herder are shown in shades of red on the left of the chart, and those with ThickSlick 6535 (TS6535) are shown on the right of the chart in shades of blue. A duplicate experiment was performed with the OP-40 herder with fresh Endicott crude.

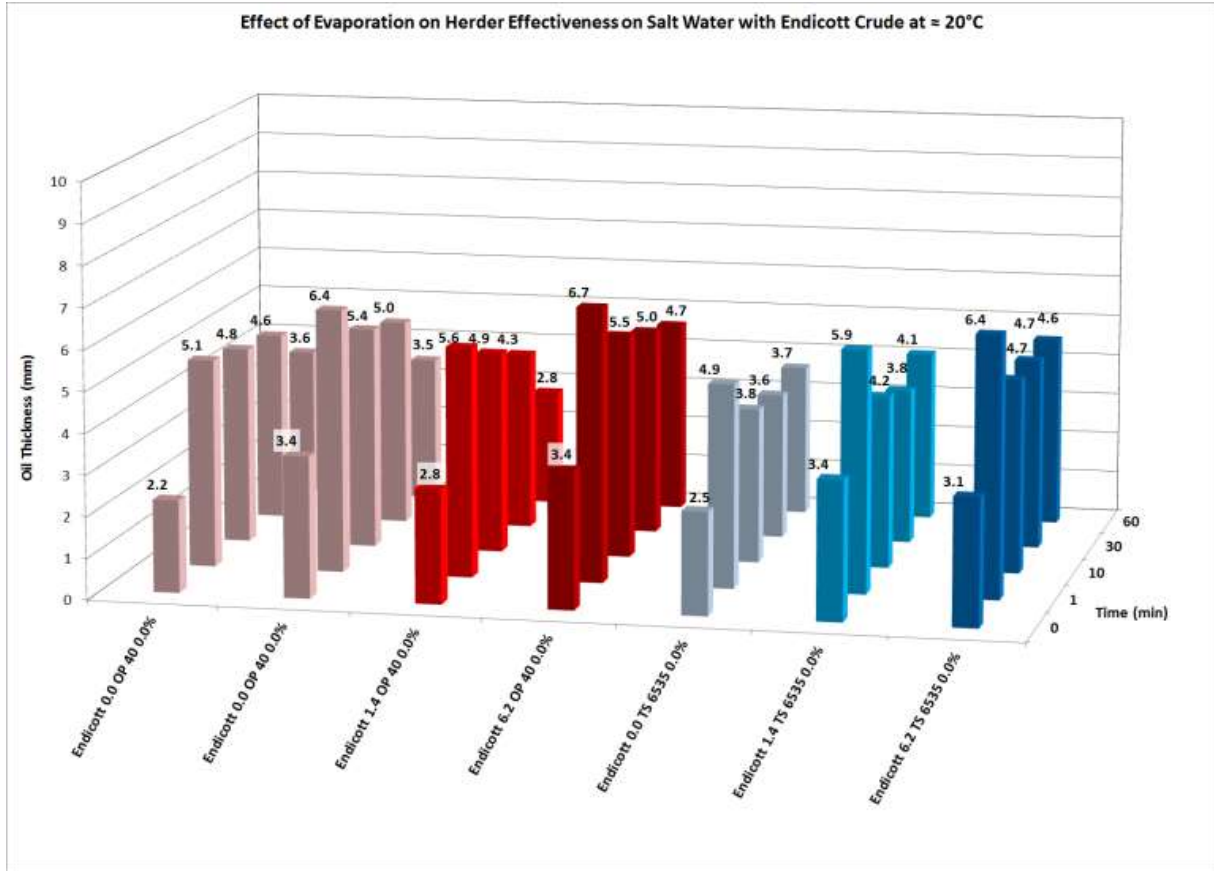
The initial spread of the Endicott crude was considerably less than for the ANS crude. Initial equilibrium thicknesses in the 2 to 3 mm range were reached in all experiments. This is as expected for this more viscous, high Pour Point crude. Despite the more viscous nature of Endicott crude, both herders were successful in contracting the equilibrium slicks to a greater thickness. The OP-40 herder was somewhat more effective with the fresh Endicott than the TS6535. There was little appreciable difference in the effectiveness of the two herders on the evaporated crude slicks. Generally, the initial herded thicknesses achieved with the OP-40 declined slowly over the time period of the tests: the slick thicknesses produced by the TS6535 declined less over the time span of the experiments.

Figure 12 shows the results from two experiments with the 1.4% evaporated Endicott crude: one experiment with water starting at 7.3° and one with 20°C water. The effect of the water temperature is quite clear: the oil on water approximately 8°C colder than its Pour Point does not spread initially, and the OP-40 herder has little effect on it. Near the end of the 7°C experiment, the water has warmed somewhat, and the gelled oil was beginning to spread out slightly. The oil on 20°C water spreads, and then is subsequently contracted by the herder.



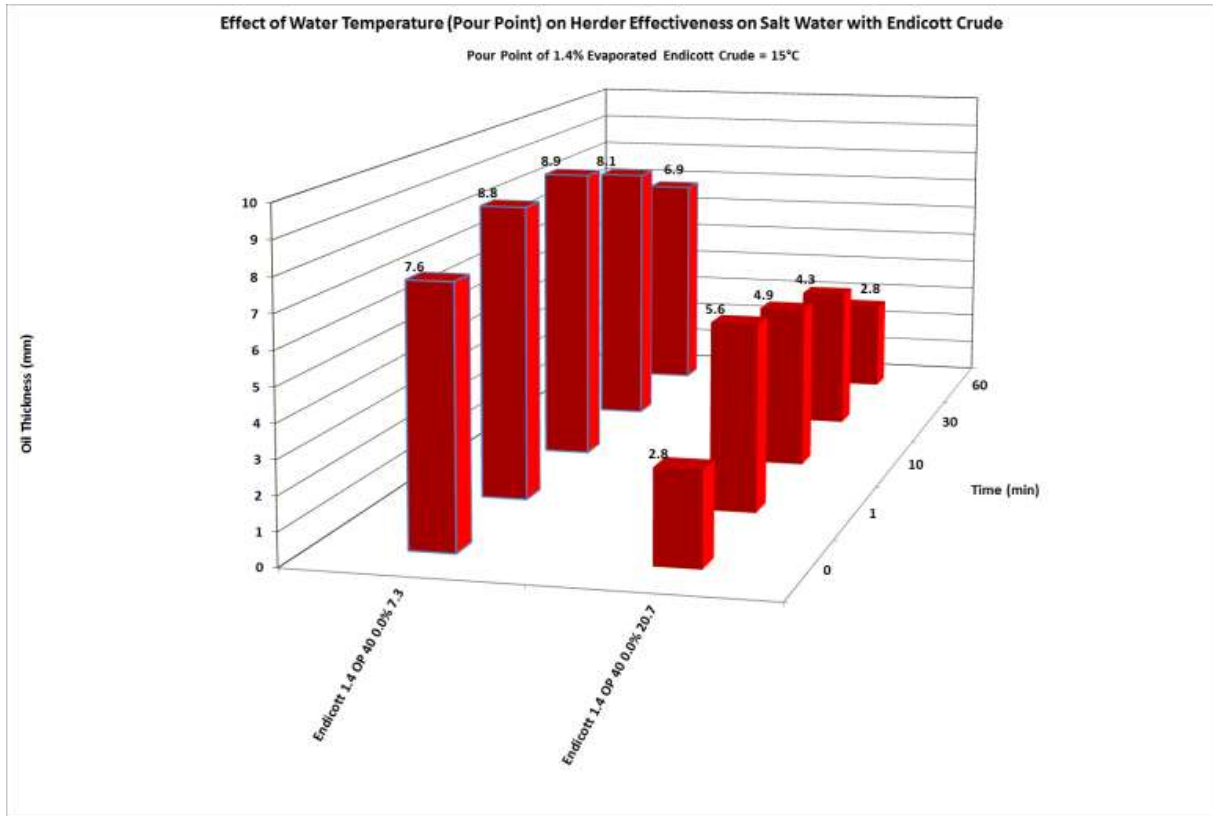
X-axis: legend XXX Y.Y ZZZZZ A.A, where XXX ≡ Letter code crude oil type; Y.Y ≡ % evaporated; ZZZZZ ≡ herder; A.A ≡ Salinity of water in ppt

Figure 10: Results of 1-m² experiments with ANS crude in slush ice.



X-axis: legend XXX Y.Y ZZZZZ A.A, where XXX ≡ Letter code crude oil type; Y.Y ≡ % evaporated; ZZZZZ ≡ herder; A.A ≡ Emulsion water %

Figure 11: Results of 1-m2 experiments with fresh and evaporated Endicott crude.



X-axis: legend XXX Y.Y ZZZZ A.A B.B where XXX ≡ Letter code crude oil type; Y.Y ≡ % evaporated; ZZZZ ≡ herder; A.A ≡ Emulsion water %, B.B ≡ T°C

Figure 12: Effect of Pour Point on herder effectiveness.

A dozen experiments were completed with emulsions of Endicott crude, varying:

- water content (20% and 50%)
- evaporation (0%, 1.4% and 6.2% evaporated)
- herder type

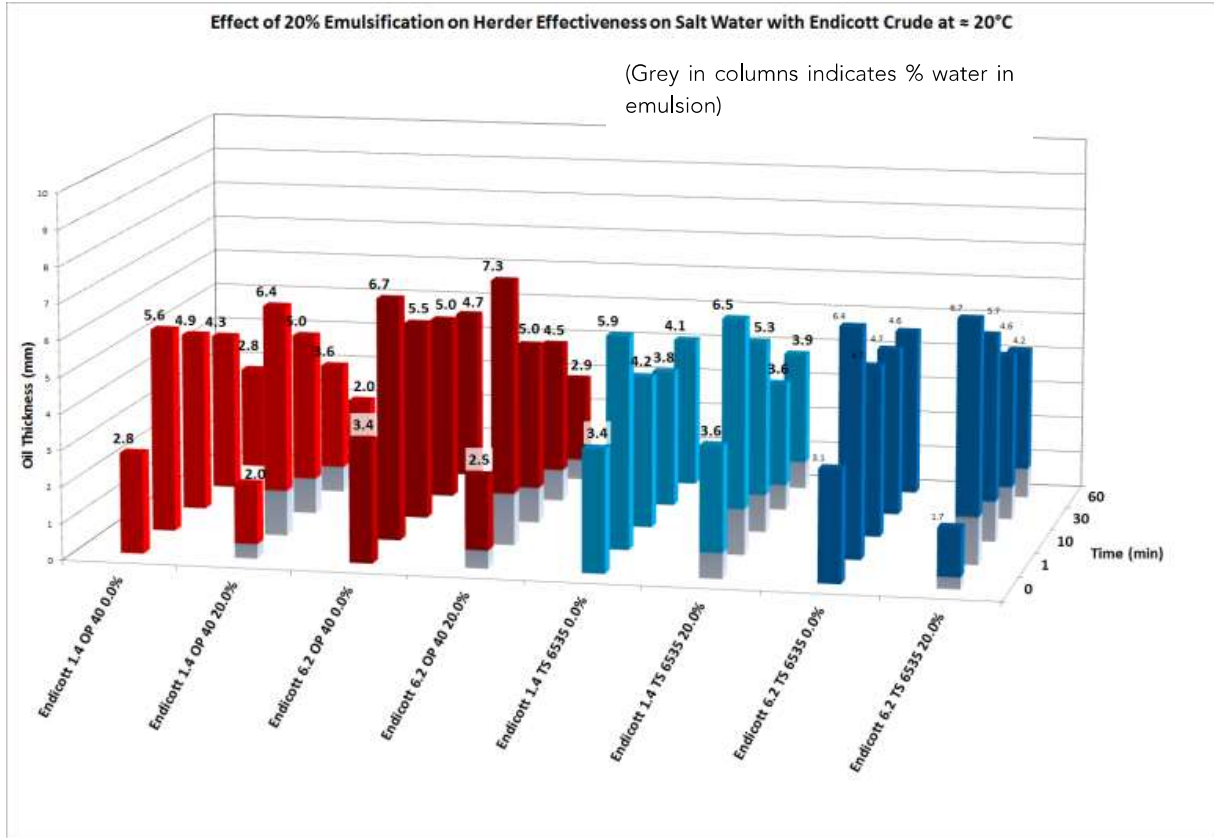
When the data from these experiments was compared, it was clear that the 50% water emulsions created with the paint mixer mounted on an electric drill had broken during the very early stages of the tests (the analysis technique employs measuring the area of the herded slick and assumes the volume of the herded slick is relatively constant: all the herded 50% emulsion slicks gave results indicating that they were twice as thick as the unemulsified slicks). It was also apparent from the data that the same had happened for the 20% water emulsions created with the fresh Endicott crude. This is consistent with the spill-related property analysis for this sample of Endicott crude (SL Ross 2008). Due to the likely instability of the emulsions, these data points were discarded as unreliable.

Figure 13 presents the results for the two herders on water-free evaporated Endicott (reproduced from Figure 12) and 20% water content evaporated Endicott crude emulsions. The emulsion data is presented as columns that are coloured 20% grey and 80% different shades of either red or blue. The general trend seems to be that the herders, though still contracting the slightly emulsified Endicott, are less efficient with emulsions than with water-free crude. It is worth noting

that 20% water content would be near the maximum ignitable, and that the initial thicknesses achieved by both herders should permit ignition of the 20% water-content emulsions.

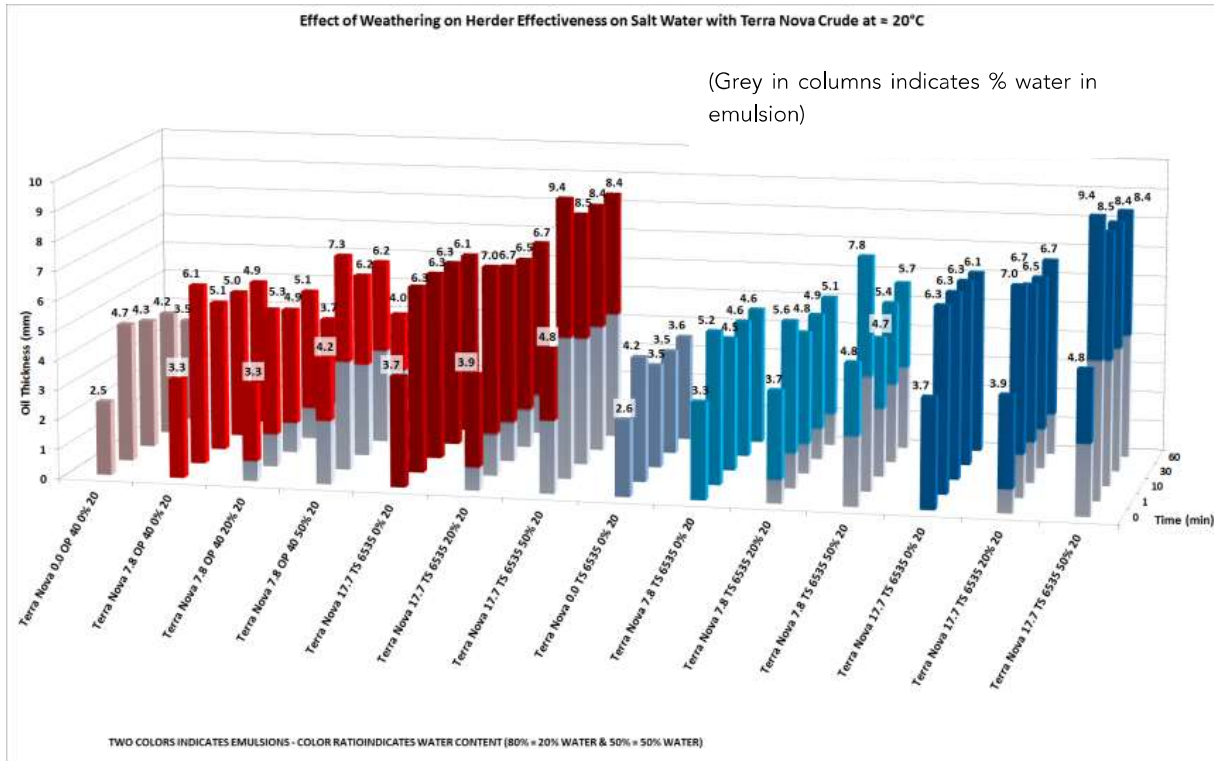
Figure 14 presents the results of herding fresh and evaporated (7.8 and 17.7% mass loss) Terra Nova crude and also the effect of 20% and 50% water content emulsification of the evaporated crude. The emulsion data is presented as columns that are coloured 20% or 50% grey (representing the water content) and 80% or 50% different shades of either red or blue, with red for OR-40 experiments and blue for TS6535 experiments.

As was the case with the Endicott crude, the fresh and evaporated Terra Nova crudes did not spread out initially as much as the ANS crude. Emulsification of the crude made it even more viscous and resistant to spreading. The OP-40 herder was slightly more effective at herding the fresh and evaporated crude at first but its effectiveness declined over the one-hour test so that by the end, both herders were containing about the same thickness of oil. As the Terra Nova evaporates, its Pour Point increases from 3°C to 21°C when it has lost 17.7% of its mass. Both herders could contract the unemulsified slicks of 17.7% evaporated crude at 20°C.



X-axis: legend XXX Y.Y ZZZZZ A.A, where XXX ≡ Letter code crude oil type; Y.Y ≡ % evaporated; ZZZZZ ≡ herder; A.A ≡ Emulsion water %

Figure 13: Effect of 20% water emulsification on herding of Endicott crude.



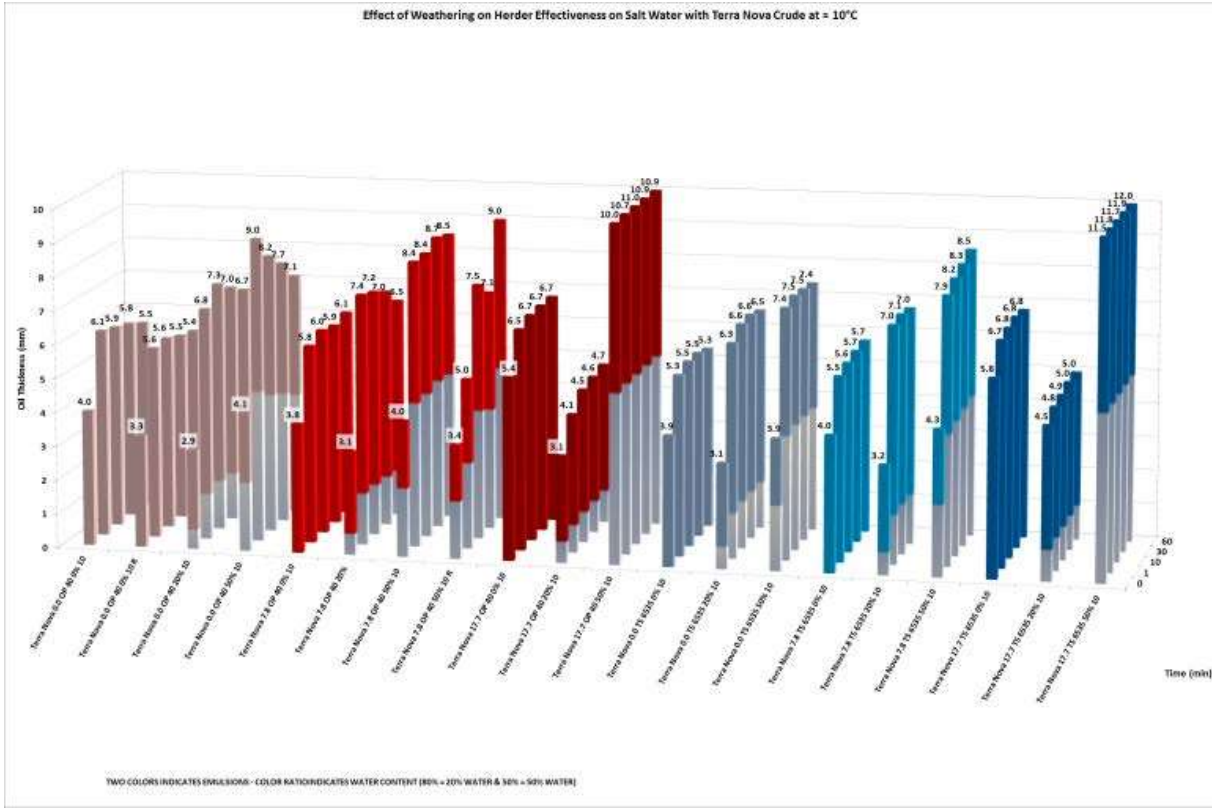
X-axis: legend XXX Y.Y ZZZZZ A.A BB, where XXX ≡ Letter code crude oil type; Y.Y ≡ % evaporated; ZZZZZ ≡ herder; A.A ≡ Emulsion water %, BB ≡ T°C

Figure 14: Effect of weathering (evaporation and emulsification) on herding of Terra Nova crude at 20°C.

Terra Nova crude forms stable emulsions even when fresh (SL Ross 2002). The data from the experiments with emulsified Terra Nova show that, even though they spread even less than the unemulsified crude initially, both herders could contract the emulsion slicks. The 20% water content slicks would likely be ignitable at the thicknesses produced, but the 50% water emulsions likely would not be ignitable, due to their high water content.

Figure 15 shows the data from the tests with Terra Nova oil and emulsions at 10°C. At this temperature, only the fresh Terra Nova crude is at a temperature above its Pour Point. Despite this both herders managed to contract emulsified slicks of gelled crude at temperatures 8° to 11°C below their Pour Points. The exception was the 50% water content emulsions of the most evaporated sample of Terra Nova, which would not spread in the first place.

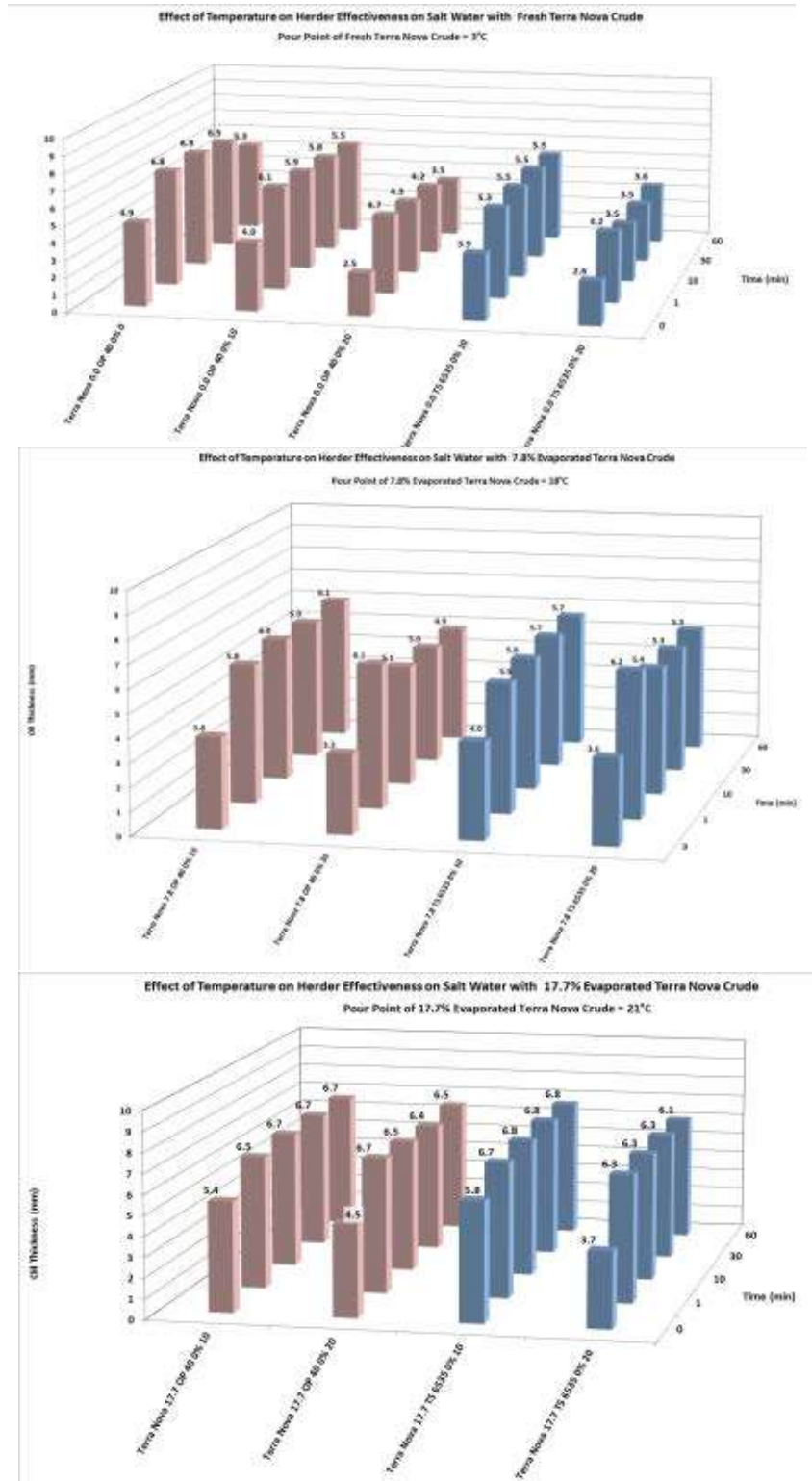
To further illustrate this, Figure 16 presents the data from experiments with fresh (top graph), 7.8% evaporated (middle graph) and 17.7% evaporated Terra Nova crude (bottom graph) at different temperatures. The test temperature is given as the last two digits of the series label on the X-axis. For the experiments with fresh Terra Nova (Pour Point = 3°C) the OP-40 can contract the slick at 0°C. Both herders appear to produce thicker slicks at colder temperatures. With the 7.8% evaporated crude (Pour Point of 18°C) and the 17.7% evaporated crude (pour Point of 21°C), the same trend continues: the herders can contract gelled slicks.



(Grey in columns indicates % water in emulsion)

X-axis: Legend XXX Y.Y ZZZZ A.A BB, where XXX ≡ Letter code crude oil type; Y.Y ≡ % evaporated; ZZZZ ≡ herder; A.A ≡ Emulsion water %, BB ≡ T°C

Figure 15: Results with Terra Nova crude at 10°C.



X-axis: legend XXX Y.Y ZZZZ A.A BB, where XXX ≡ Letter code crude oil type; Y.Y ≡ % evaporated; ZZZZ ≡ herder; A.A ≡ Emulsion water %, BB ≡ T°C

Figure 16: Herder Effectiveness at temperatures above and below Pour Point Terra Nova Crude

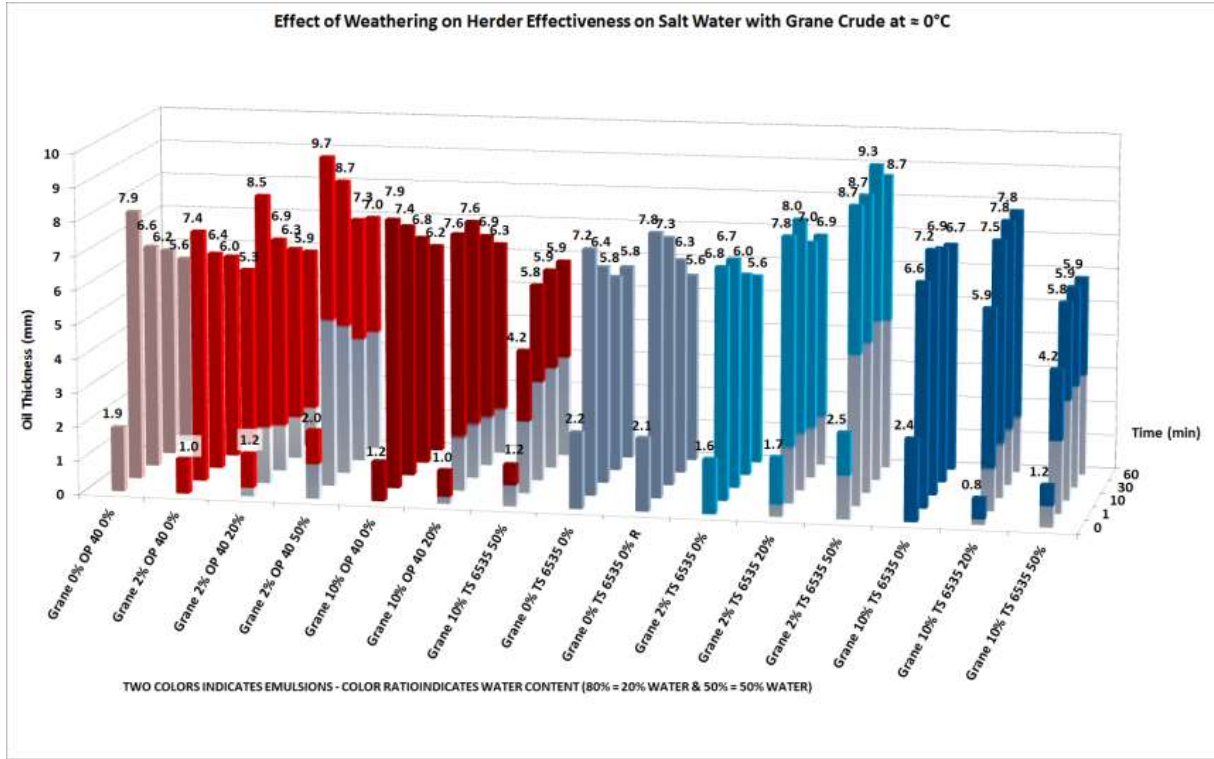
Figure 17 shows the results from the 1-m² experiments with the Grane crude at 0°C. It was sparged to 2% and 10% evaporative loss, and stable emulsions with 20% and 50% water content were prepared (Strom 2013, Brandvik *et al.* 2010). The emulsion data is presented as columns that are coloured 20% or 50% grey and 80% or 50% different shades of either red or blue, depending on the herder and water content.

The Grane crude spread more initially than either the Terra Nova and Endicott crudes, but still not quite as much as the ANS crude. The initial equilibrium thicknesses for the unemulsified Grane crude were in the 1 to 2 mm range.

Both herders proved to be very effective with the Grane crude and emulsions, generally achieving herded thicknesses in the 5 to 7-mm range. As has been noted before, the thickness of slicks herded with OP-40 tended to decline slowly over the one-hour test. The thickness of Grane slicks herded by the TS6535 tended to decline less, or not at all. Evaporated Grane crude formed fairly stable emulsions at 0°C and both herders appeared to contract these slicks as well or better than the water-free slicks. The 50% water content slicks of the 10% evaporated Grane crude were not thickened as well as the less “weathered” slicks by either herder. Stable emulsions of weathered crude with a 50% water content are generally considered non-ignitable.

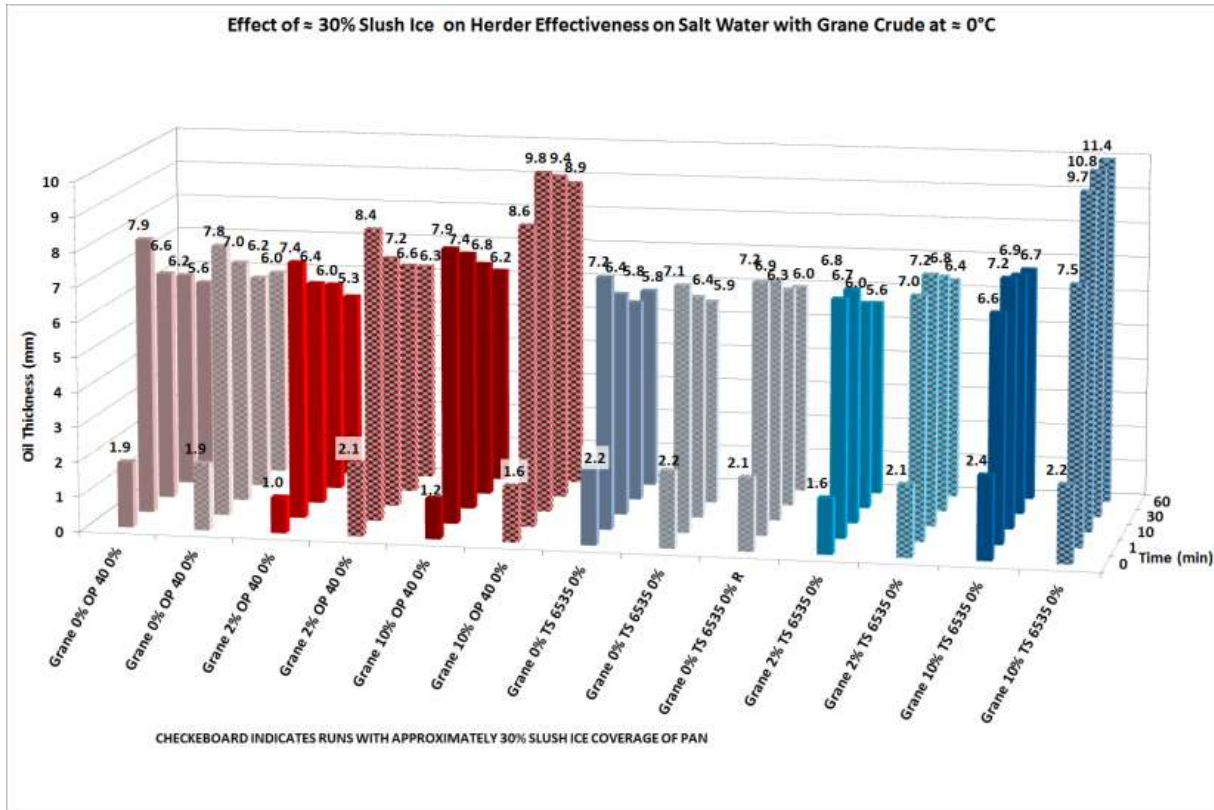
Figure 18 presents the results of the experiments involving slush ice (simulated by adding a bag of crushed ice cubes to the water in the pan at the beginning of the experiment). As with the same experiments with the ANS crude, the presence of the slush ice restricts the initial spreading of the oil.

Both herders were effective on the fresh and both evaporated Grane crude samples in slush ice. Initially, the OP-40 herder was somewhat more effective than the TS6535. At the end of the tests the OP-40 herded slicks in slush ice had respread slightly, declining in thickness to the levels maintained by the TS6535 herder.



X-axis: legend XXX Y.Y ZZZZZ A.A, where XXX ≡ Letter code crude oil type; Y.Y ≡ % evaporated; ZZZZZ ≡ herder; A.A ≡ Emulsion water %

Figure 17: Experimental results with fresh, evaporated and emulsified Grane crude at 0°C.



X-axis: legend XXX Y.Y ZZZZZ A.A, where XXX \equiv Letter code crude oil type; Y.Y \equiv % evaporated; ZZZZZ \equiv herder; A.A \equiv Emulsion water %

Figure 18: Effect of slush ice on herding of Grane crude.

4.2.2.2 Dynamic Film Performance Experiments

The Dynamic Film Performance (DFP) experiments were done with 0°C, 35‰ salt water in a small environmental chamber to maintain the water temperature near freezing during the 1-hour procedure.

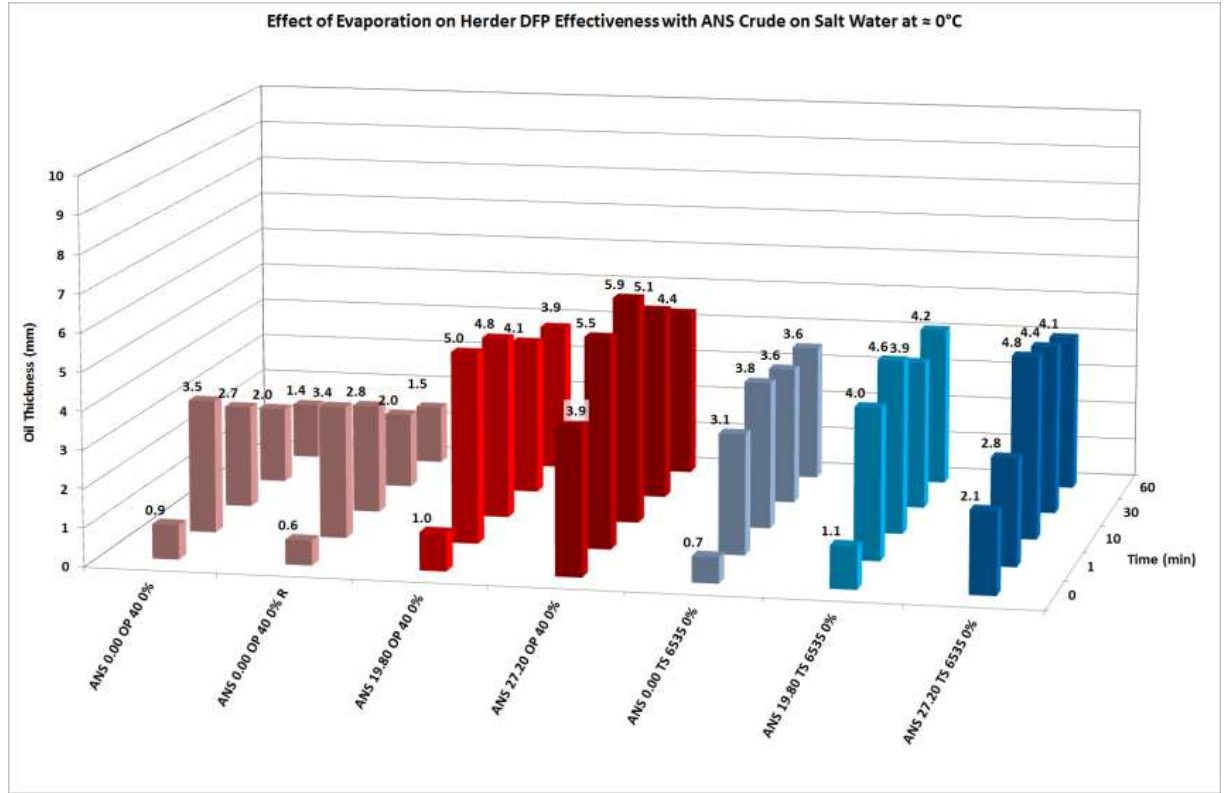
The test matrix included:

- ThickSlick 6535 and OP-40
- Three crude oil types (Alaska North Slope, Grane and Terra Nova – Endicott was excluded due to its very high pour point);
- Fresh and two degrees of evaporation for each crude; and,
- Two emulsion water contents (20% and 50%) with fresh Terra Nova and 10% evaporated Grane.

Figure 19 shows the results with the ANS crude. The experiments with the OP-40 herder are shown in shades of red on the left of the chart, and those with ThickSlick 6535 (TS6535) are shown on the right of the chart in shades of blue. A duplicate experiment was performed with the OP-40 herder with fresh ANS crude. ANS crude would not form a sufficiently stable emulsion at the degrees of evaporation used in these experiments (SL Ross 2014).

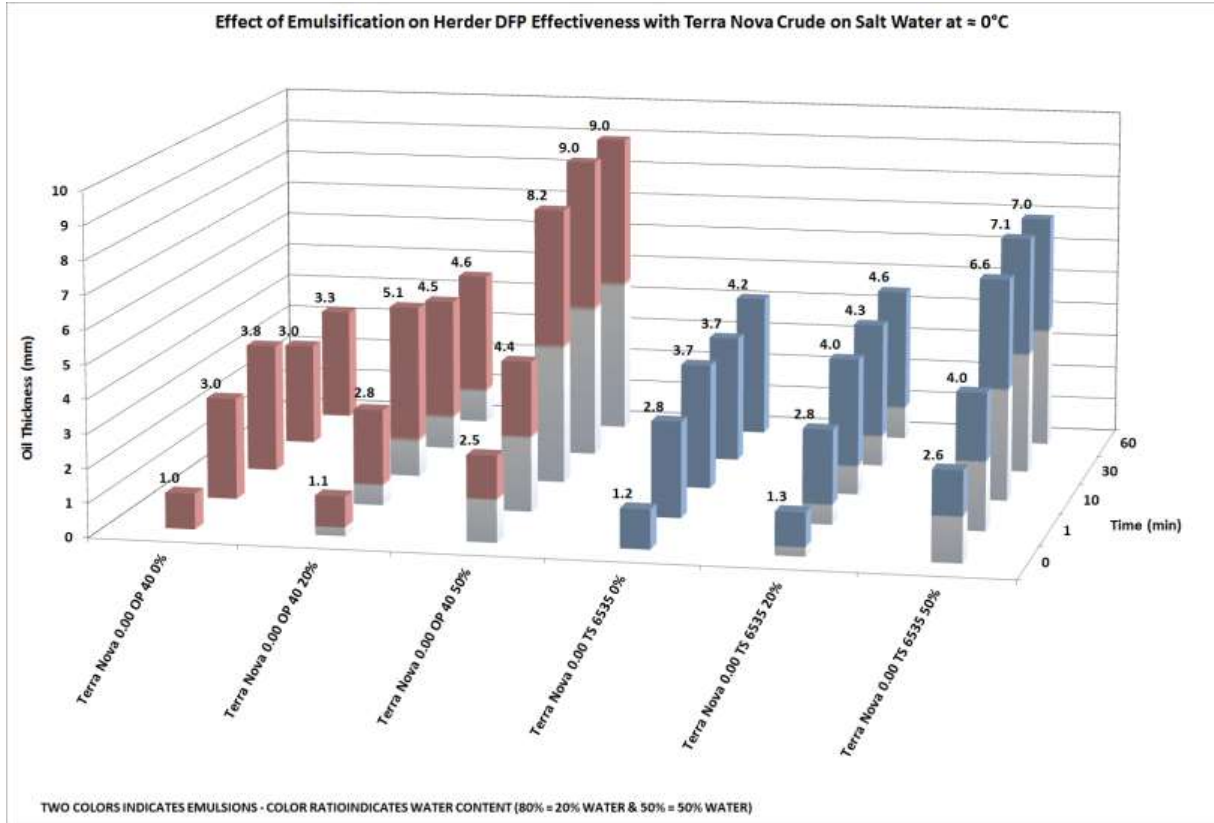
The ANS crude spread to an initial thickness of approximately 0.5 to 1.5 mm. The OP-40 herder appeared to work better on the fresh ANS than the TS6535, achieving an initial herded thickness of 3.5 mm vs. 3.1 mm; however, the OP-40 herded slick slowly spread out over the one-hour time span of the experiment, whereas the TS6535 maintained its initial herded thickness. This was the general trend with the evaporated ANS experiments as well. Both herders produced better results in the DFP test apparatus with the evaporated ANS crude than the fresh. Comparison of Figure 19 with Figure 9 (ANS on 0°C salt water in the 1-m² experiments) shows that the simulated swell wave conditions in the DFP apparatus generally reduce the effectiveness of the herders; however, both can still maintain an ignitable slick thickness of crude for the one-hour experiment duration.

Figure 20 presents the effects of emulsification of fresh Terra Nova crude on herder effectiveness in the DFP test. Evaporated Terra Nova samples were not tested in the cold chamber due to their high Pour Point (18° and 21°C). Even though the Pour Point of the fresh Terra Nova crude is 3°C, both herders were effective in contracting the slicks in the DFP apparatus. In comparison, in the 1-m² pan tests, the OP-40 was only slightly effective with Terra Nova at 0°C (Figure 16). This difference is likely due to the wave energy imparted to the slick and herder in the DFP apparatus which prevents a fully-developed precipitated wax matrix from forming gelled oil. This aids the herder in contracting the slicks. Both herders contracted emulsified slicks of fresh Terra Nova crude. The OP-40 was slightly more efficient than the TS6535. Mixing energy imparted by the DFP apparatus is likely responsible for the better performance of the herders at 0°C than was observed in the 1-m² apparatus at 10°C (Figure 15).



X-axis: legend XXX Y.Y ZZZZZ A.A, where XXX \equiv Letter code crude oil type; Y.Y \equiv % evaporated; ZZZZZ \equiv herder; A.A \equiv Emulsion water %

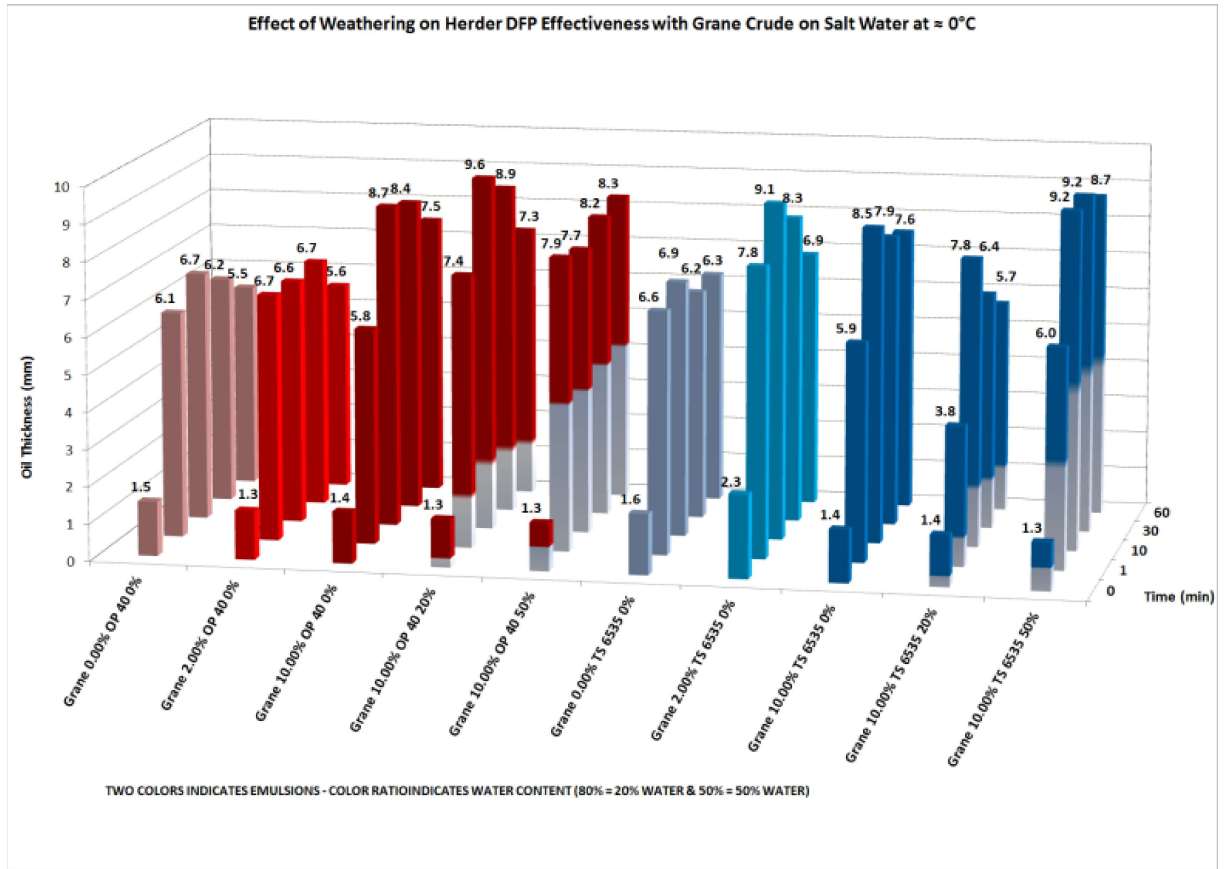
Figure 19: DFP experiment results with fresh and evaporated ANS crude at 0°C.



X-axis: legend XXX Y.Y ZZZZZ A.A, where XXX ≡ Letter code crude oil type; Y.Y ≡ % evaporated; ZZZZZ ≡ herder; A.A ≡ SaliEmulsion water %

Figure 20: Effect of emulsification on herder effectiveness with fresh Terra Nova crude in a DFP.

Figure 21 shows the results from the DFP experiments with fresh, and weathered Grane crude. The initial equilibrium thicknesses for the slicks were in the 1- to 2-mm range. Both herders caused significant contraction of all the test slicks. Herded slick thicknesses were consistently in the 6 to 9 mm range, regardless of herder, evaporation or emulsification. These thicknesses were as good as, or slightly better than those achieved in the static 1-m² pan experiments (Figure 17), particularly for the emulsified Grane crude samples. The mixing energy imparted to the system by the DFP tests is likely responsible.



X-axis: legend XXX Y.Y ZZZZZ A.A, where XXX \equiv Letter code crude oil type; Y.Y \equiv % evaporated; ZZZZZ \equiv herder; A.A \equiv Emulsion water &%

Figure 21: DFP test results with fresh, evaporated and emulsified Grane crude at 0°C.

4.2.2.3 10-m² Pool Tests

The ANS and Grane crude samples tested in the 10-m² pool were selected based on the results of the 1-m² and DFP experiments. Some experiments involved slush ice and some Grane crude experiments involved emulsions.

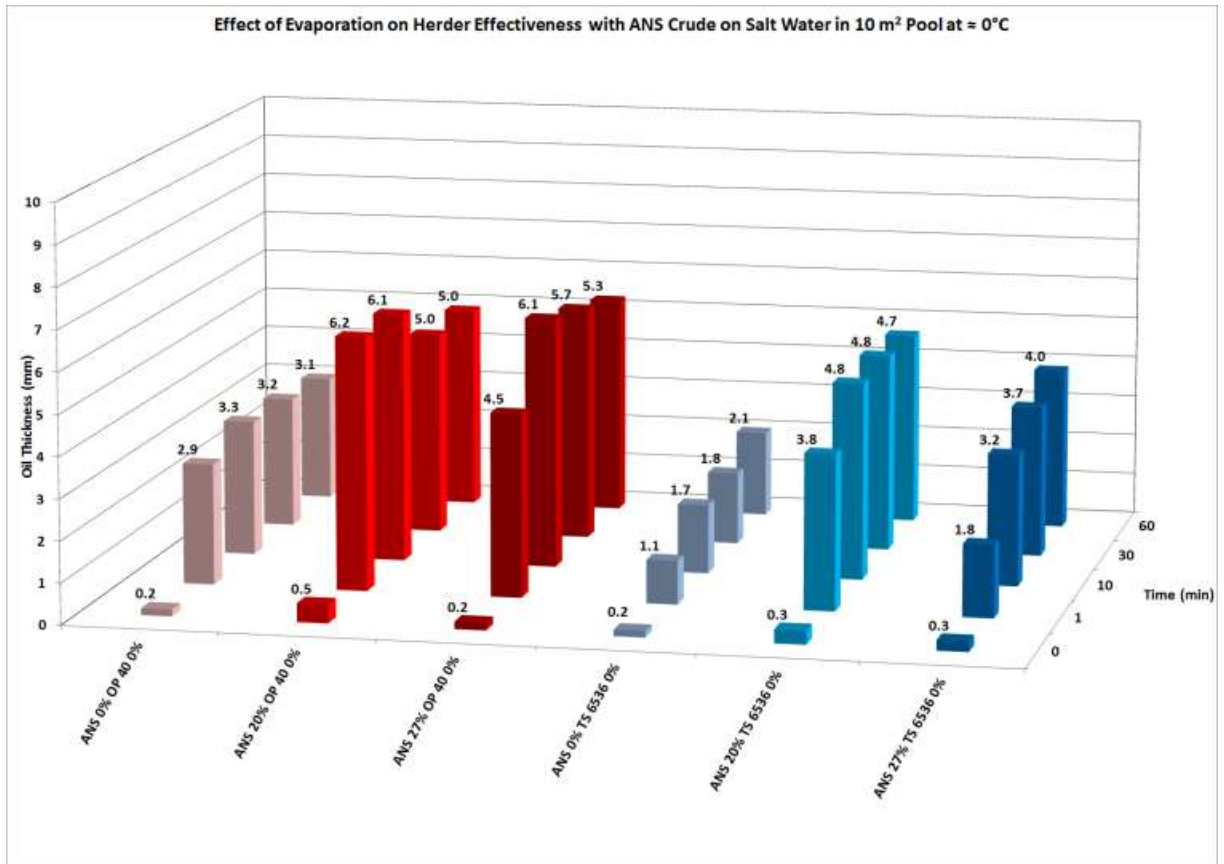
Figure 22 shows the results of the experiments with the two herders with fresh and evaporated ANS crude at 0°C. Because the test pool was laid out on the concrete floor of the laboratory, once it was filled with near freezing salt water from the refrigerated wind/wave tank, the water temperature would slowly increase over time, often warming up to 5 to 10°C by the end of the experiment.

The initial equilibrium thickness of the ANS crude samples ranged from 0.2 to 0.5 mm, about half of the values measured in the 1-m² experiments (Figure 9). This is likely due to the 1-m² experiments involving 500 mL of crude on a 1 m² area of water while the 10-m² experiments used 1 L of crude on a 10 m² water surface. The oil in the 10-m² pool could spread more before edge effects caused it to stop.

The OP-40 worked better than the TS6535 with the fresh and two degrees of evaporation of the ANS crude. In general, the contracted slick thicknesses measured for both herders were quite similar in the 10-m² pool and in the 1-m² pans.

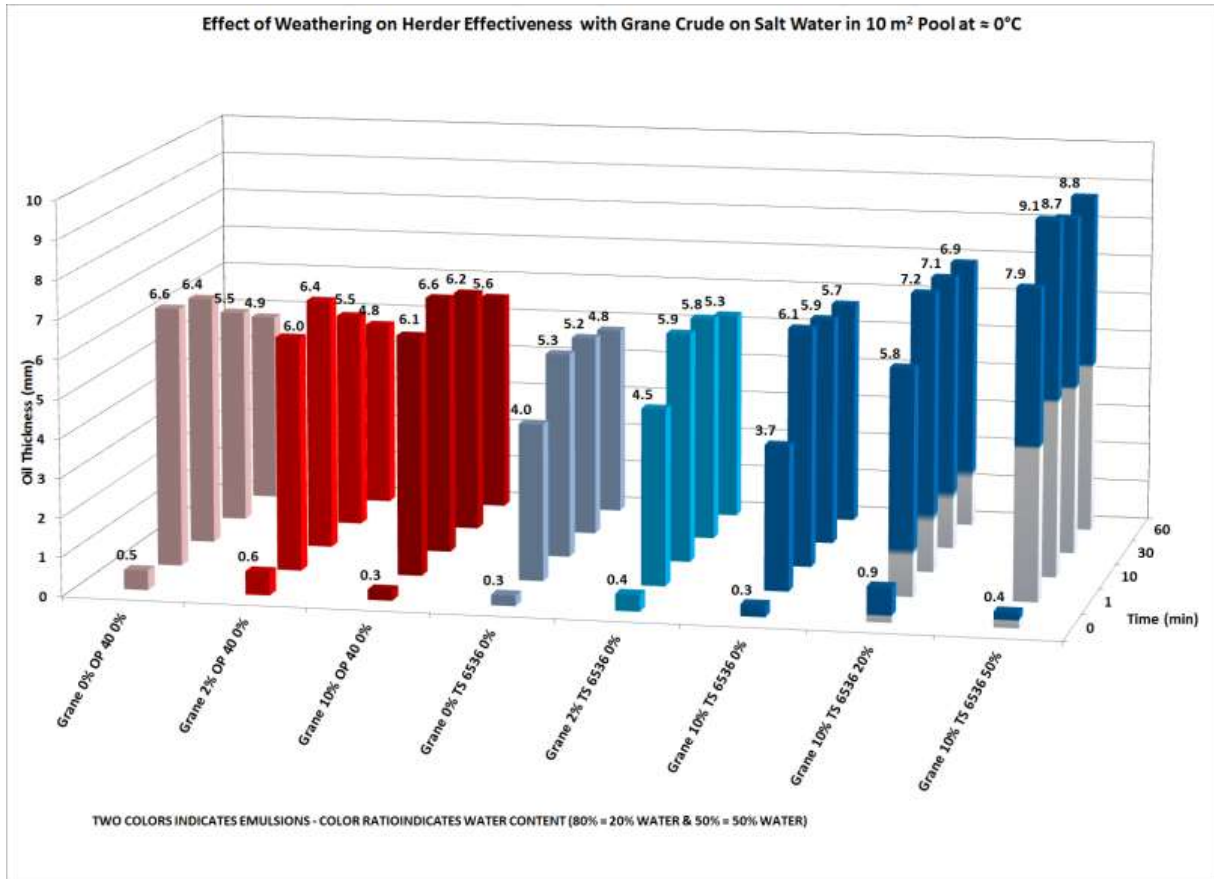
Figure 23 shows the results of the experiments with the Grane crude, including some emulsions. As was the case for the experiments with ANS crude, the initial equilibrium slick thicknesses were considerably lower in the 10 m² pool than in the 1 m² pan. Both herders were effective with this crude. The OP-40 produced slightly thicker slicks initially, but by the end of the one-hour experiment the OP-40 slicks had thinned to the same thicknesses achieved with the TS6535. The herded water-free slick thicknesses in these tests were generally the same as in the 1-m² pans.

Two emulsions produced with the 10% evaporated Grane crude were also tested in the 10-m² pool using the TS6535 herder. Both the 20% water and 50% water emulsions were effectively herded by the TS6535. The 10-m² result was nearly identical to the 1-m² result; however, the 50% water result was appreciably better than in the 1-m² pan. This may be the result of an unstable emulsion, rather than better performance by the herder.



X-axis: legend XXX.Y.Y ZZZZZ A.A, where XXX ≡ Letter code crude oil type; Y.Y ≡ % evaporated; ZZZZZ ≡ herder; A.A ≡ Emulsion water %

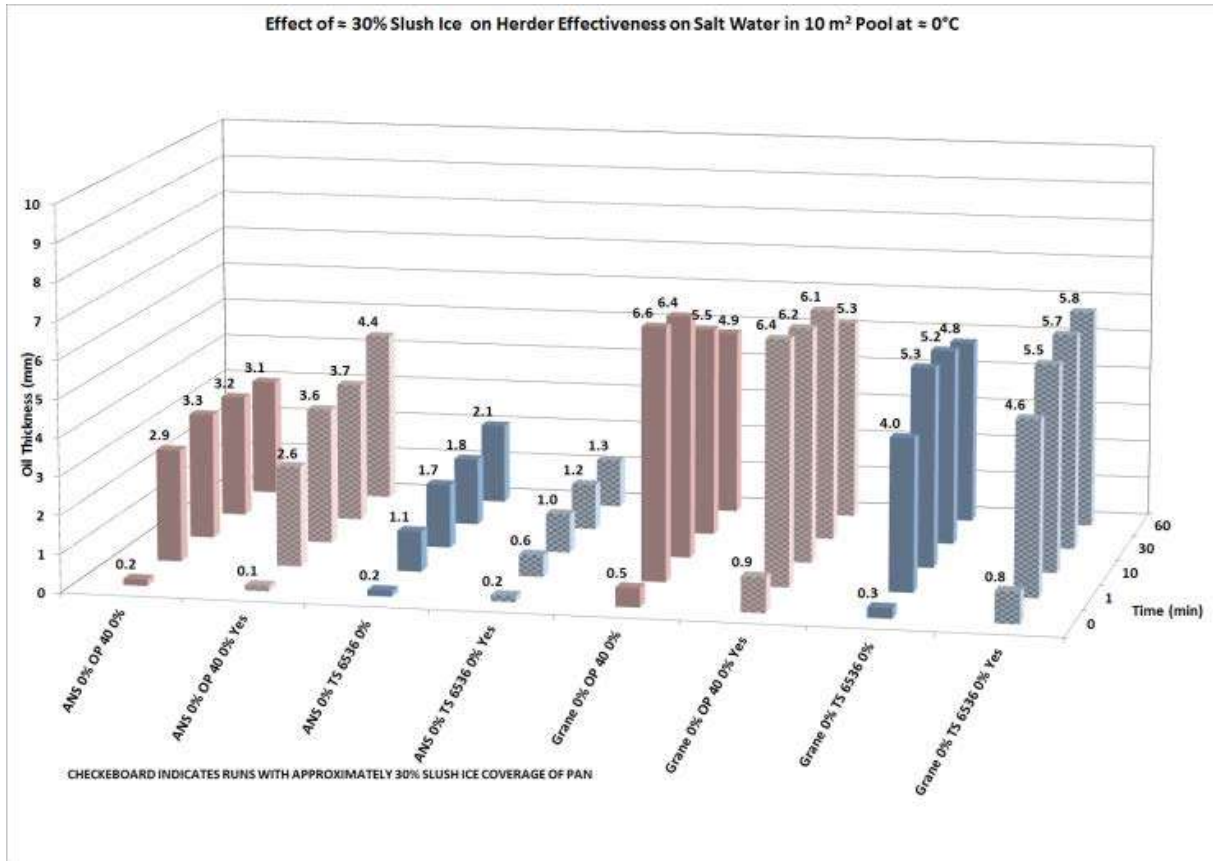
Figure 22: Results of experiments with ANS crude and emulsions in the 10-m² pool.



X-axis: legend XXX Y.Y ZZZZ A.A, where XXX \equiv Letter code crude oil type; Y.Y \equiv % evaporated; ZZZZ \equiv herder; A.A \equiv Emulsion water %

Figure 23: Results of experiments with Grane crude and emulsions in the 10-m² pool.

Figure 24 presents the results of the experiments with fresh ANS crude and fresh Grane crude in the 10-m² pool with slush ice at a coverage of approximately 30%, compared to the data from open water tests. As was noted with the previous experiments, the initial equilibrium thickness of the oils was appreciably less in these tests than in the 1-m² series (Figures 10 and 18). Both herders managed to contract the slicks in the presence of slush ice. The OP-40 herder worked better in the slush ice than the TS6535, and also appeared to work better in slush ice than on open water. Both herders, but particularly TS 6535, appeared to be considerably less effective with the fresh ANS than with the fresh Grane crude on both open water and in slush ice.



X-axis: legend XXX.Y.Y ZZZZZ A.A, where XXX ≡ Letter code crude oil type; Y.Y ≡ % evaporated; ZZZZZ ≡ herder; A.A ≡ Emulsion water %, Yes = slush ice

Figure 24: Results of experiments with Grane crude in 30% slush ice

4.2.2.4 Wind/Wave Tank Experiments

The oil and herder combinations tested in the SL Ross wind/wave tank were selected based on the results of the 1-m² DFP and 10-m² experiments. Fresh and two evaporated ANS crude samples and fresh Grane crude were used for the six burn experiments with the two herders and fresh Grane and ANS crudes were used in the monolayer persistence experiments, with the two herders.

Figure 25 presents the oil removal efficiencies measured in the six test burns. One burn with each fresh oil and no herder were conducted in a floating metal ring containing 400 mL of oil, as a control. The ANS control burn resulted in a 67.7% removal and the Grane control burn removed 61.2% of the crude. Theoretically, the 3.2 mm initial slick thickness (400 mL in a 40 cm diameter burn) should result in a 68.6% removal efficiency. The test burn with the fresh and evaporated ANS crude herded with OP-40 produced removal efficiencies of 58.5% for the fresh ANS, 46.1% for the 19.8% evaporated ANS and 55.7% for the 27.2% evaporated ANS. For each of the experimental burns using herder, the slicks would expand slightly as the flames spread over the oil, then contract again as the flames began to extinguish. The lower efficiency measured for the 19.8% evaporated ANS is believed to be due to experimental error and not a significant difference.

The burn with fresh ANS crude herded by TS6535 resulted in a removal efficiency of 49.4%. The experiment with Grane crude herded with OP-40 produced a removal efficiency of 59.4% and the one involving fresh Grane herded by TS6535 resulted in a removal efficiency of 39.7%. There appears to be a trend of higher oil removal efficiency with OP-40 than with TS6535 in these experiments.

Four experiments in the wind/wave tank involved placing 500 mL of fresh crude in a monolayer of herder that had been applied to the water surface earlier, then increasing the steepness of the waves generated by the wave board (by increasing the frequency). The oil was not ignited. The first experiment involved a slick of fresh ANS crude herded by TS6535. At the least energetic wave setting (10 cm wave height with a 2-s period) the herded slick would contract and expand as a wave crest passed under it. As wave periods decreased, the herded ANS slick narrowed and divided into smaller slicklets. These slicklets were still constrained by the herder. When the wave period was eventually reduced to 0.6 s, spilling breakers quickly broke up the slicklets into small bits of oil surrounded by sheen. It was clear that the monolayer of herder was being rapidly dispersed into the water by these breaking waves.

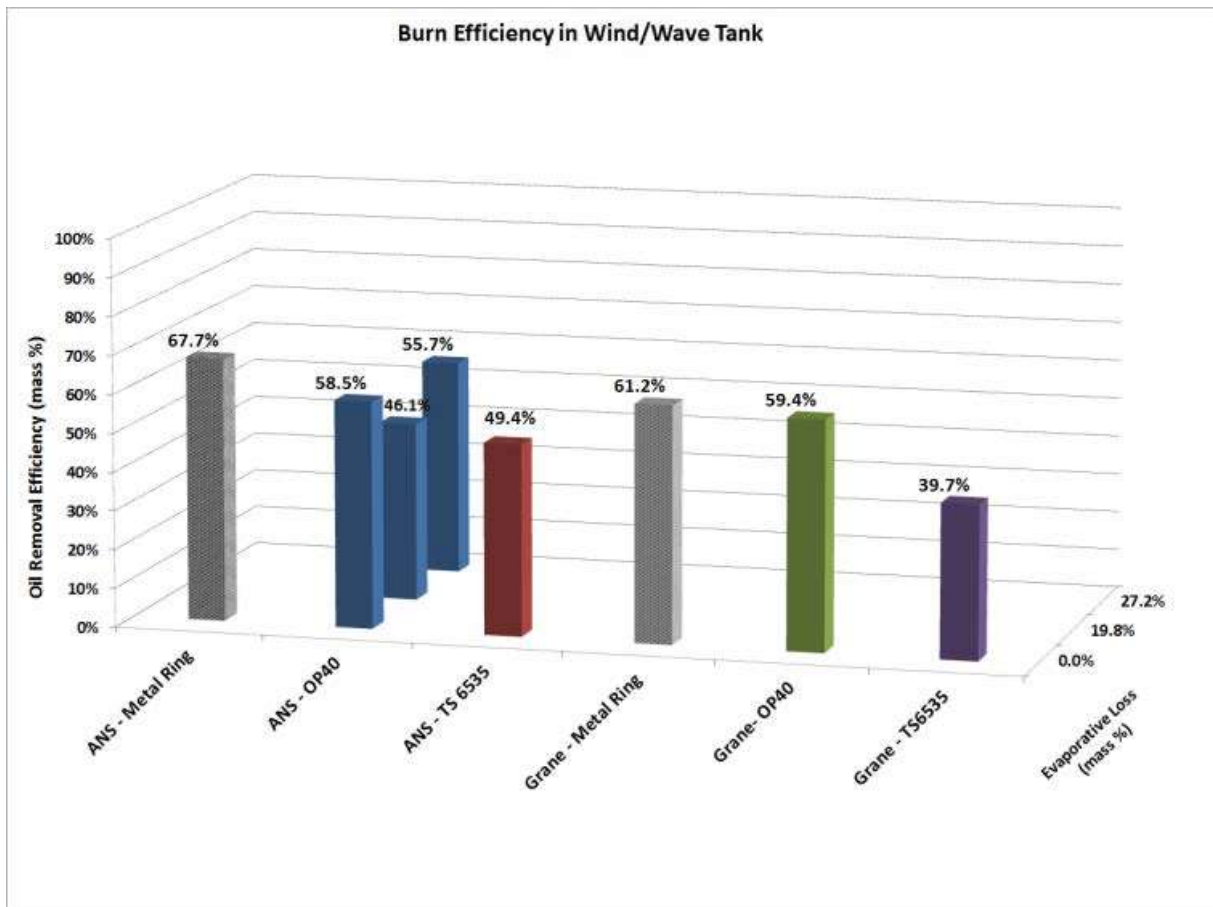


Figure 25: Burn efficiency experiments in the SL Ross wind/wave tank.

The second experiment involved fresh ANS crude herded by OP-40. The slick behaviour observed was the same as with the TS6535: contacting and expanding at the longest period; herded slick dividing into smaller slicklets, then when the waves began to break, the formation of smaller,

sheening bits of slick. There was no noticeable slick behaviour difference between the two herders.

The third wave test involved fresh Grane crude herded by OP-40. For the lower wave energies, the Grane slicks behaved as the ANS slick herded by OP-40 had. When the wave period was reduced to 0.6 s, the breaking waves quickly broke the slicklets up into small bits, but less sheening was observed. This may have been an artefact of the different crude oil, not the herder or waves. In the final experiment (fresh Grane herded by TS6535) similar behaviour was noted: when the wave period was reduced to 0.6 s, the slick rapidly formed stringy tendrils which, after 2 minutes had separated into many small bits. Again, much less sheen was noted than with the equivalent experiment with ANS crude.

4.3 Larger-scale Experiments (28.5 m²) at CRREL

4.3.1 Methods

Two experimental test pools were set up on levelled sand in the refrigerated Research Area at CRREL. The air temperature was maintained at -4°C. Each test pool was constructed using lumber to be approximately 5.3 m x 5.3 m x 15 cm (Figures 26 and 27). Each pool frame was laid on white cloth to permit good discrimination between oil, ice and water in the overhead photos and video. Polyethylene film was used on top of the white sheeting and clamped to the sides to provide clean containment for each experiment. Prior to filling the pool for an experiment, the plastic film used to line the pool was rinsed with clean tap water to ensure it did not release surfactants that might affect the spreading of the oil. Cold salt water (35 ppt) was used to fill the test pools to a depth of 2.5 to 5 cm, enough to ensure the entire bottom of the pool was covered with at least 2 cm of water. The pool water surface tension was measured before each experiment. If the IFT reading was less than 60 mN/m it was necessary to sweep the pool water surface with sorbent and resample.

An overhead digital SLR camera and a digital video camera mounted over the centre of each pool were used to record the spread of the oil and subsequent herding for later analysis. Each experiment lasted for approximately one hour. At the end of each experiment, the crude oil was sorbed off the water surface, the water pumped to storage and the plastic liner replaced to ensure a pristine test pool for the next test. The test oil was ANS crude, from CRREL supplies provided by IOGP. This particular crude was also used in the SL Ross laboratory tests. Fresh, 17.5% evaporated and 29.4% mass evaporated crude were used at CRREL. The amount of oil used for each experiment was measured by weighing the bucket before and after the pour.

Four experiments were conducted with 20% water content emulsions of the 29.4% evaporated ANS. The emulsions were mixed in the plastic bucket with a paint mixer attached to an electric drill just before each experiment. Eight of the 18 experiments conducted over the two-week test period involved slush ice, created by shovelling loose, natural snow onto the pool water surface just prior to a test (Figure 28).

The oil was released from the edge of a pool using a spill plate (Figure 29) to prevent the oil from impinging on the bottom of the pool and allowed to spread to equilibrium (determined visually from



Figure 26: Lined test pools on sand in Research Area at CRREL.



Figure 27: Test pool filled with salt water with slush ice.



Figure 28: Shovelling loose natural snow onto the water surface to create slush ice.



Figure 29: Pouring crude oil from bucket down spill plate onto water surface.

poolside). The oil volume used was nominally 7.5 L. The overall surface area of the test pool was 28.5 m². Thus, the oil could spread to as thin as 0.25 mm initially. Just before the oil was released to spread, the overhead digital video was started and the digital SLR set to take a picture every 10 seconds and save it to a laptop (Figure 30). Once the oil has stopped spreading (based on visual observations from poolside), herder was added drop-wise to the water surrounding the slick using a disposable syringe. The target application rate was 150 mg/m², yielding a nominal amount of 4 g (4 mL) per test. The syringe was weighed before and after the application to measure the amount of herder used. Time- and date-stamped overhead digital videos (encompassing each of the test pools and surface scale markers) were recorded continuously for each one-hour test. Part of the signal was used to create a DVD recording of the test, and part was saved as a discrete image at a fixed rate to a Web site for backup. Still images were taken every 10 seconds from the overhead digital SLR cameras. These were used to get images 1, 2, 5, 10, 20, 40, and 60 minutes after the herder application ended, and digitally processed to calculate oiled areas.

Hand-held digital SLR cameras were also used to record the testing from poolside. The air and water temperature were monitored and recorded. Figures 31 through 33 show example images and Figure 34 demonstrates how the images were processed to determine oil area and thus average slick thickness. At the end of each experiment, the crude oil was sorbed off the water surface, the water pumped storage and the plastic liner replaced to ensure a pristine test pool for the next test.



Figure 30: Experiment image acquisition for video (left) and digital SLR (right)



Figure 31: Pouring oil onto water on test pool at start of test.



Figure 32: Oil spread to equilibrium thickness in slush ice.

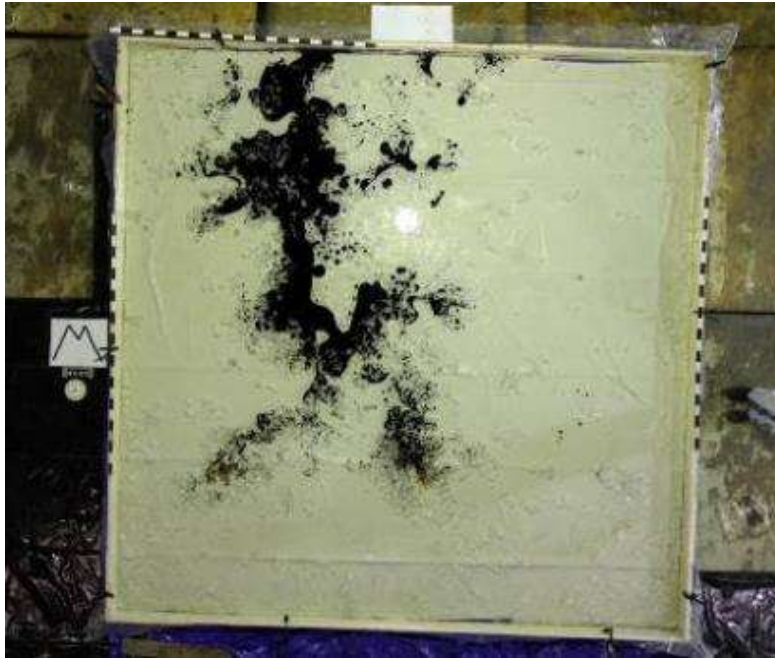


Figure 33: Herded oil in slush ice 3 minutes after herder application.

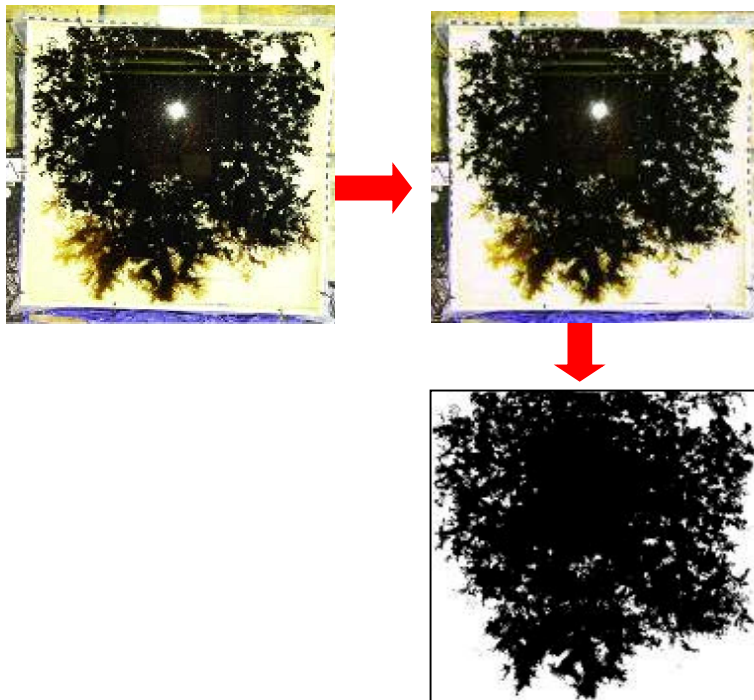


Figure 34: Image analysis process: image distortion corrected, image converted to B&W, black pixels counted by software, number of pixels converted to area from photo scale, oil volume used to calculate average thickness from area.

4.3.2 Test Matrix

Test matrix variables included:

- One crude oil (ANS)
- Fresh, two degrees of evaporation and one emulsion (20% water)
- One oil volume (7.5 L)
- No ice and slush ice (30%)
- Two chemical herders (ThickSlick 6535 and Siltech OP 40) applied at 150 mg/m² or 4 mL/test)

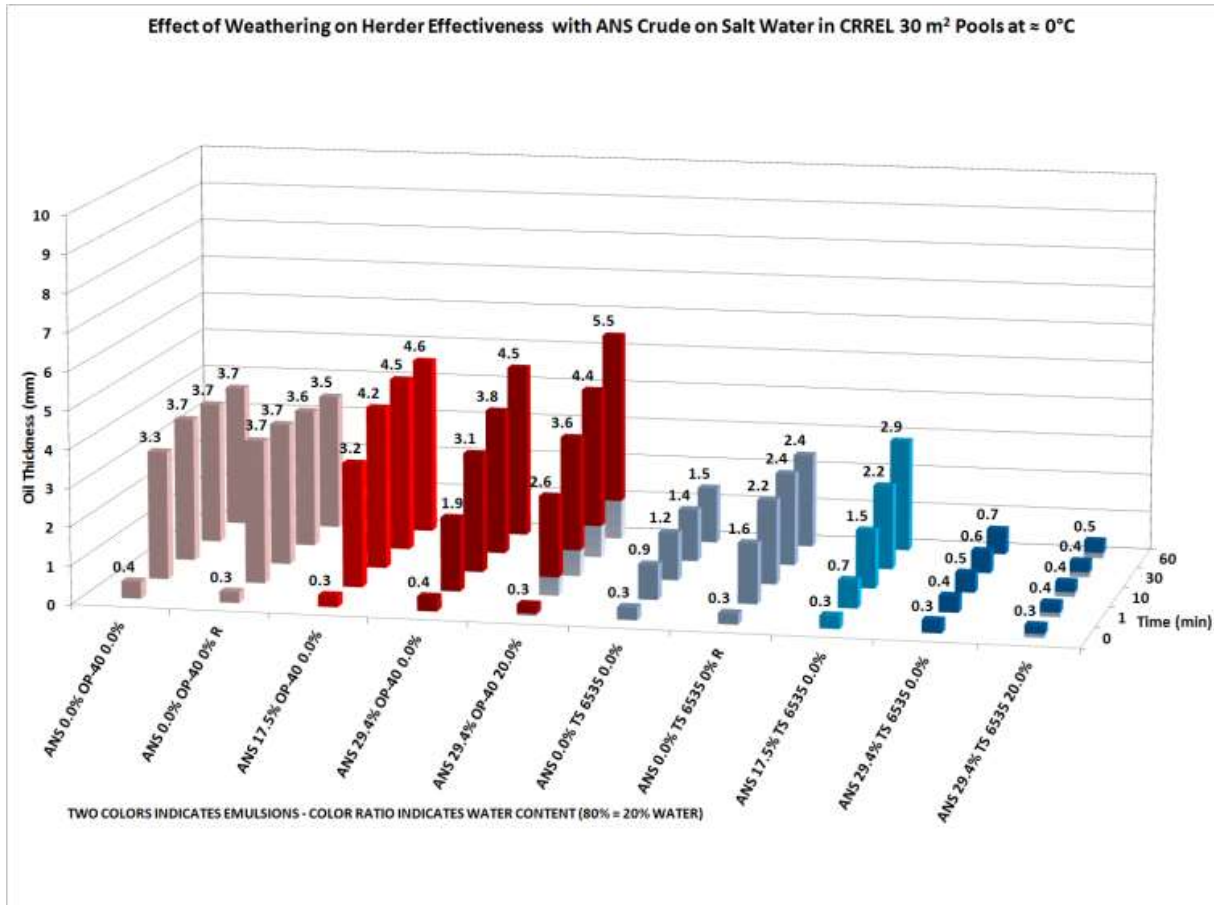
Varying all of the baseline conditions (1 x 4 x 1 x 2 x 2) gives 16 individual tests. Two duplicate tests were also conducted. Table 3 shows the experiments completed in March of 2015.

Table 3 Experiments at CRREL

Test #	ANS Weathering	Herder	Ice	Oil Volume (L)	Air T (°C)
Prepared pools					
Equipment setup and checks					
1, 2	0%	Both	none	7.5	-4
3, 4	0%	Both	slush	7.5	-4
R1, R2	0%	Both	none	7.5	-4
5, 6	17.5%	Both	slush	7.5	-4
7, 8	17.5%	Both	none	7.5	-4
9	29.4%	TS6535	none	7.5	-3
10	29.4%	OP-40	none	7.5	-4.5
11,12	29.4%+ 20% emulsion	Both	none	7.5	-4
13,14	29.4%	Both	slush	7.5	-4
15,16	29.4% + 20% emulsion	Both	slush	7.5	-4
Demobilize					
Cleanup					

4.3.3 Results

Figure 35 presents the results from the experiments on open water in the 28.5 m² pools at CRREL. Two duplicate experiments were done. Initial equilibrium thicknesses for the fresh, weathered and emulsified slicks were consistently 0.3 to 0.4 mm on the salt water in the pools. The OP-40 herder again performed better than the TS6535, achieving thicknesses on par with those measured in the 10-m² experiments in the SL Ross laboratory (Figure 22). The results obtained with the 20% water emulsion of the 29.4% evaporated ANS may be an artefact of the emulsion breaking over the time frame of the test. All the OP-40 herded slicks would have been ignitable 10 minutes after herder application.

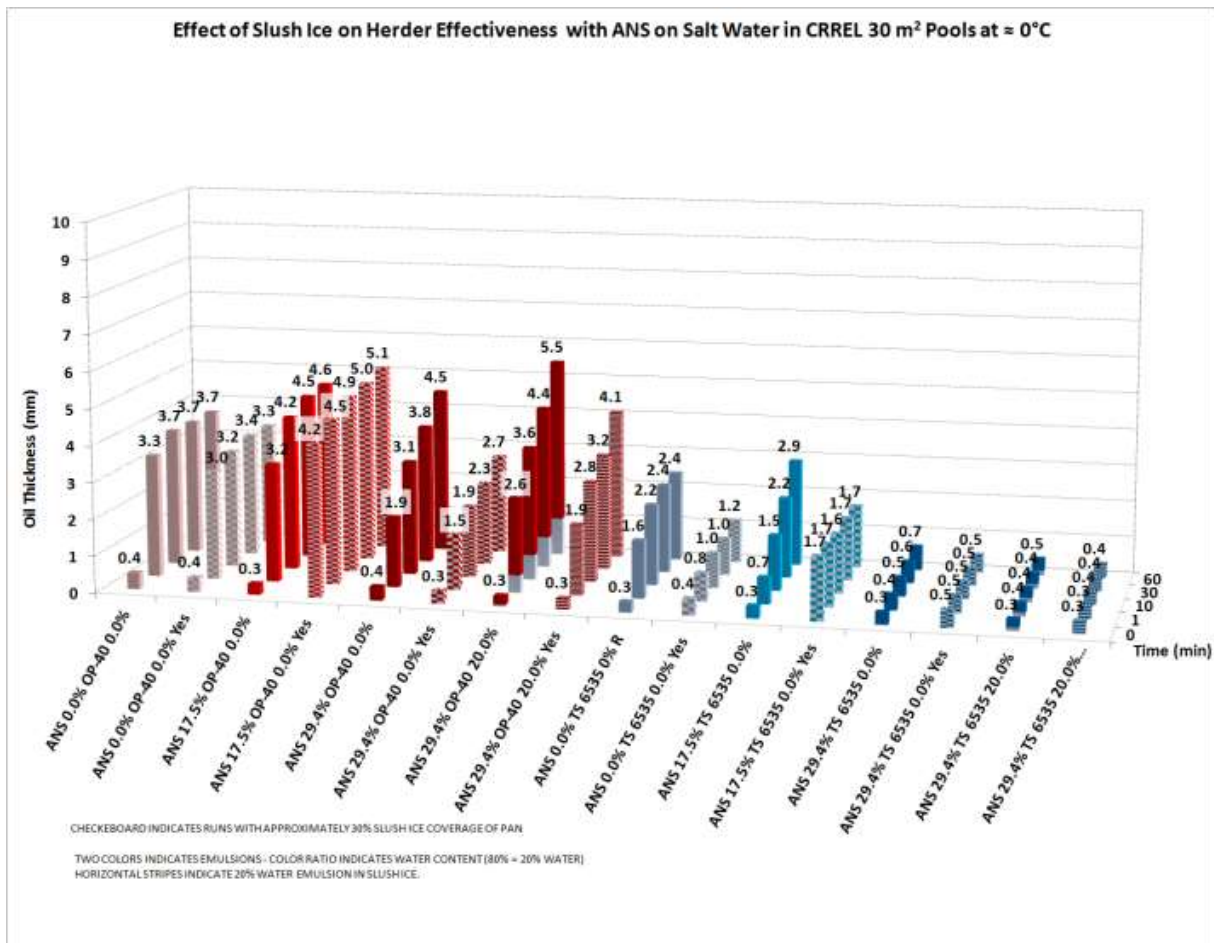


X-axis: legend XXX Y.Y ZZZZZ A.A, where XXX ≡ Letter code crude oil type; Y.Y ≡ % evaporated; ZZZZZ ≡ herder; A.A ≡ Emulsion water %, R ≡ Repeat

Figure 35: Experimental results on open water in 28.5 m² pools at CRREL.

The performance of the TS6535 was particularly poor: appreciably less efficient than in the SL Ross experiment series (see for example Figure 22 for the 10-m² pool experimental results). The experiments at CRREL used a different aliquot of the ThickSlick than those at SL Ross, and it is possible that the sample sent to CRREL was not properly formulated or mixed. After the first few tests, the steel can containing the TS6535 was kept on a warm transformer in the Research Area control room and shaken vigorously before each 4mL was withdrawn with a syringe for a test. The duplicate experiment with the TS6535 and the fresh ANS was done after warming and shaking the can of herder; whereas the original experiment was the first conducted. There was an appreciable difference between the two tests, with the duplicate giving results much closer to those obtained in the SL Ross 10-m² pool. The 17.5% evaporated ANS was herded by the TS6535, but much more slowly and less effectively than in the SL Ross tests. Neither the 29.4% evaporated slick nor the 20% emulsified slick were appreciably herded by TS6535 over the one-hour experiments at CRREL. These tests were done after the change was made to warm and shake the can of TS6535. In the 10-m² experiments at SL Ross, TS6535 herded 27.2% evaporated ANS to a final thickness of 4 mm (Figure 22).

Figure 36 compares the results of the tests in slush ice with the equivalent tests in open water. Note that the checkerboard pattern on the chart bars indicates an experiment that involved slush ice. In the first two tests with slush ice (ANS 17.5% evaporated with TS 6535 and ANS 17.5% evaporated with OP-40) the surface coverage of slush ice was much higher than intended, perhaps as high as 90 to 100%. In both of these experiments the oil was prevented from spreading to its usual initial equilibrium thickness by the ice, and the ice prevented the herder from reaching the edge of the slicks. The OP-40 performed well in the 30% slush ice cover, with the fresh and 17.5% evaporated crude, albeit taking a little longer to thicken the slicks and achieving a lower one-hour herded thickness compared to the equivalent slicks in open water. The 29.4% evaporated slick was consistently thinner than the equivalent in open water, but did achieve an ignitable thickness after 30 minutes. The same was true for the emulsified 29.4% evaporated crude. Emulsion instability may be playing a role in the results for the tests with ANS emulsions. The TS6535 was not nearly as effective as the OP-40 in slush ice: it barely contracted the fresh oil to an ignitable thickness after one hour and had no effect on the 17.5%, 29.4% or emulsion slicks.



X-axis: legend XXX.Y.Y ZZZZZ A.A, where XXX ≡ Letter code crude oil type; Y.Y ≡ % evaporated; ZZZZZ ≡ herder; A.A ≡ Emulsion water %, R ≡ Repeat, Yes ≡ Slush ice

Figure 36: Effect of slush ice on herder effectiveness at CRREL.

5. RESEARCH ON FATE AND EFFECTS OF CHEMICAL HERDERS

By DCE - Danish Centre for Environment and Energy, Aarhus University Technical University of Denmark and SL Ross Environmental Research

5.1 Goal

The goal of these experiments was to increase the knowledge about the environmental fate and effects of two commercially-available herders ThickSlick 6535 (TS6535) and Siltech OP-40 (OP-40) in the polar marine environment, as very little is known regarding the environmental effects of the chemical herders. For TS6535 and OP-40 only preliminary standard tests for biodegradability and toxicity are available (SL Ross and DCE 2014). Knowledge regarding environmental impacts is needed to support a well-founded Net Environmental Benefit Analyses (NEBA) prior to advising decisions-makers if and when herders can be allowed as the collecting agent in an ISB operational response situation. In the NEBA process pros and cons of the different response tools are compared, and thus the NEBA is used to be able to make the best choices of response methods, in order to minimize the impacts of the oil spill on the environment in an acute oil spill situation.

The experiments involved two different crude oils (both fresh and emulsified). Small-scale herding and burning experiments were carried out in the laboratories of DTU (Technical University of Denmark) for investigation of the physical fate of the herders during burning. The samples from the experiments were analysed for the herder content at the laboratories of DCE (Danish Centre for Environment and Energy, Aarhus University). Environmental effects studies included toxicity testing and bioaccumulation of the two herders on high Arctic copepods (*Calanus hyperboreus*), the potential biodegradation in Arctic conditions and the impacts on Arctic seabird feathers (Thick-Billed Murre and Common Eider). All the species were collected in Greenland and part of the experiments were also conducted in Disko Bay, Greenland and completed in the laboratories of DCE. All the experiments were conducted in the period from 2014 – 2015.

Additional burning experiments were carried out at the SL Ross Laboratory in Ottawa. These experiments involved two different fresh crude oils and weathered samples of one crude to determine if there was a difference in mechanically contained burns versus herded oil burns from a smoke plume perspective. Samples were analysed by Environment Canada's Air Quality Research Division – Emissions Research and Measurement Section analytical laboratory. Their air quality research facility is also located in Ottawa, Canada, and includes an emissions testing laboratory capable of conducting detailed emissions measurements.

5.2 Burning experiments at DTU

Laboratory experiments were carried out in the Crude Oil Flammability Apparatus (COFA) in the laboratories of DTU for generation of samples for further analyses (see Chapters 5.3 and 5.5) but also in order to study the thickening effect of the two herding agents. The herders, SilTech OP-40 (OP40) and ThickSlick 6535 (TS), were applied around slicks of two fresh crude oils, Alaska North Slope (ANS) and Grane, and their corresponding emulsions with 25% water content. Moreover, the ignition, burning mechanisms and related parameters were studied. In addition to the main experiments, where the oil slicks were herded (post-herding application) followed by ignition, a series of three different experiments were carried out. In the first series, the herding capability was analysed for application of the herder prior to the oil application (pre-herding

application). In the second series, the duration of the herding ability was studied (long-term effect of herder application after the oil spread). Finally, the last series consisted of control experiments where the oil was confined by a Pyrex Glass Cylinder prior to ignition followed by ignition (i.e. there was no use of herder).

The experiments were completed in the period from November 2014 – April 2015.

5.2.1 Methods

5.2.1.1 Experimental set-up

Several parameters were studied systematically through a series of herding and ISB experiments related to the ignition and combustion of the oil (see Figure 37). The environmental aspects of the herder were further studied in the laboratories at DCE (see chapters 5.3 and 5.6).

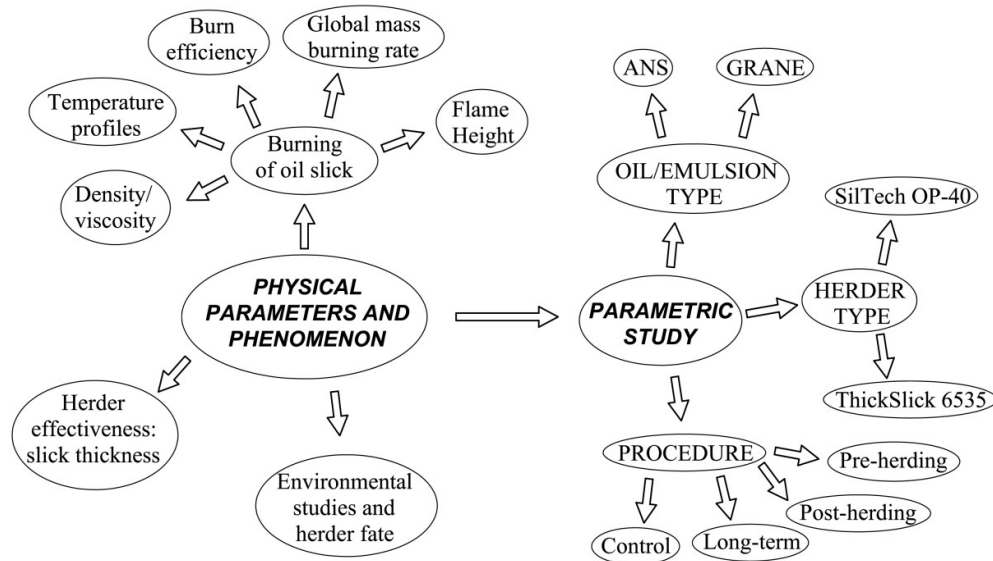


Figure 37: General overview of the parameters and phenomena studied herein.

Two crude oils were investigated: Alaska North Slope (ANS) and Grane. The latter is an asphaltenic crude oil with a high content of resins and it is expected to form stable emulsions (Fritt-Rasmussen 2010). ANS is a medium grade crude oil, with lower density and viscosity than Grane. Also, 25% water-in-oil emulsions were studied for both crude oils. The emulsions were made by the rotating flask technique, a modified technique based on Mackay & Zagorski (Mackay and Zagorski 1982). The measured physical properties are displayed in Table 4 for both crude oils and emulsions.

Table 4: Measured physical properties of two crude oils and their corresponding 25% water-in-oil emulsions.

<i>Properties</i>	<i>Oil type</i>		<i>Emulsion type¹</i>	
	ANS	Grane	ANS	Grane
Bulk density [g/cm ³]	0.871	0.918	0.894	0.945
Kinematic viscosity [mm ² /s]	12.3	143.2	19.3	208.4
Dynamic viscosity [mPa.s]	10.7	131.4	17.4	195.7

The properties of the water-in-oil emulsions are average values obtained from several measurements performed in the Viscometer SVM 3000 apparatus.

The general nomenclature code used for the experiments is depicted in Figure 38.

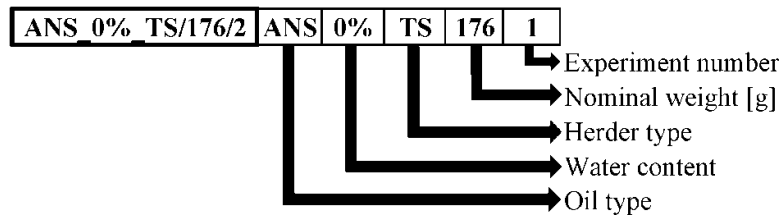


Figure 38: Nomenclature codification used for the experiments. The presented example is for ANS crude oil, no emulsion (0%), herded with Thick Slick (TS) and there were 176 grams of oil. Finally, the experiment was the first in the series.

Figure 39 provides a general overview of the entire experimental procedure and Figure 40 illustrates the experimental set-up in the laboratory. Each procedure is described in details for the four types of experiments conducted: post-herding (main experiments), pre-herding, long-term and control.

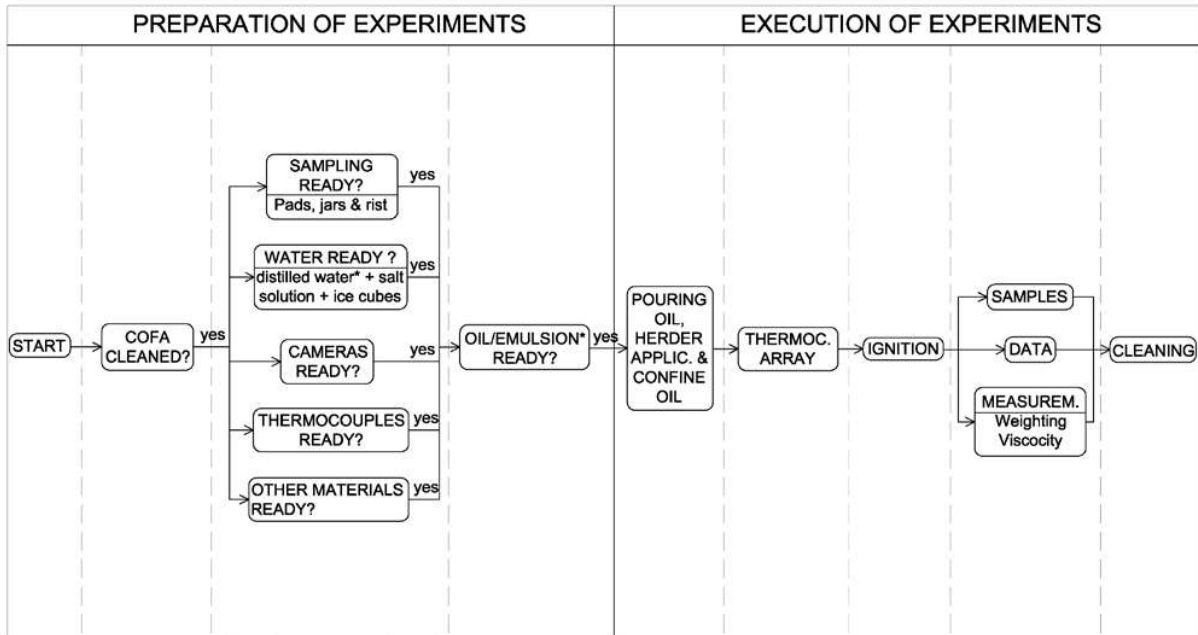


Figure 39: Activity flowchart covering all the experimental procedures.

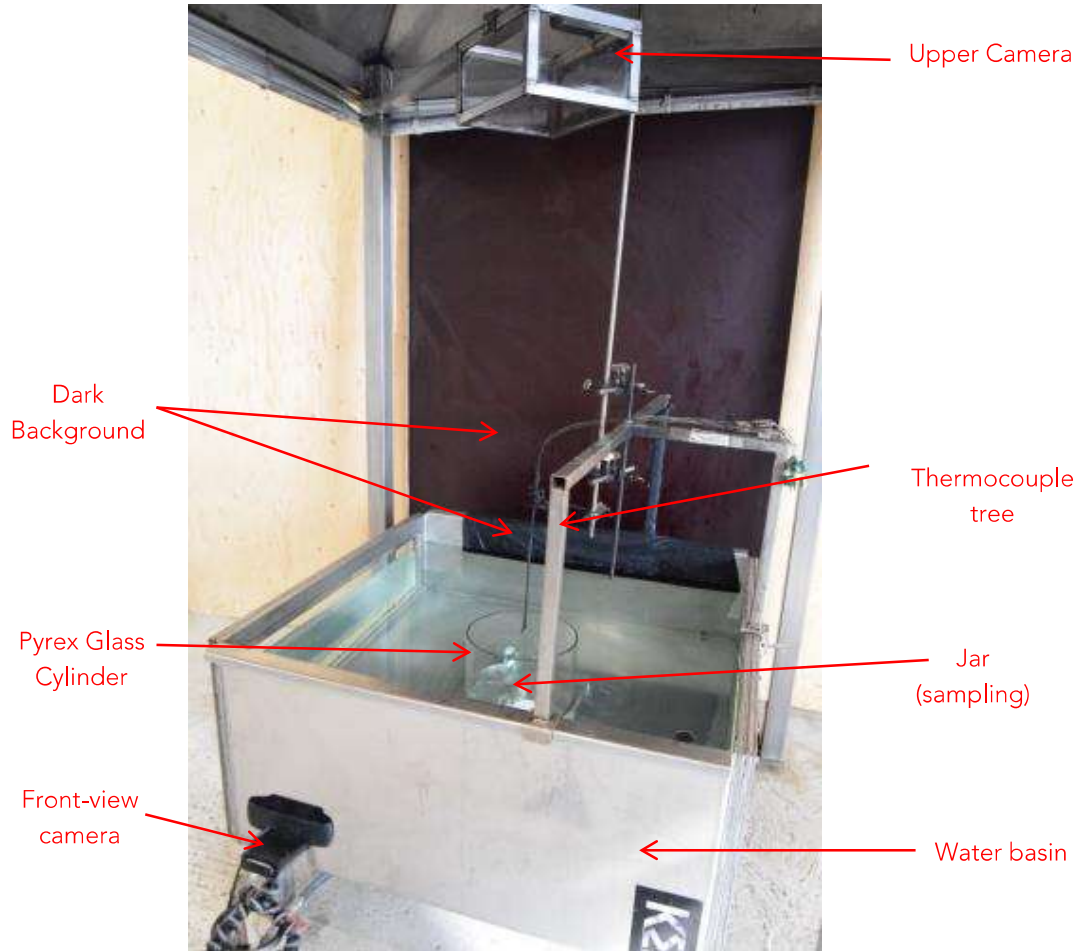


Figure 40: COFA; experimental rig for in-situ burning experiments.

5.2.1.2 Density and viscosity measurements

The density and viscosities (kinematic and dynamic) of the fresh crude oils, fresh water-in-oil emulsions, and the post-burn residues were measured by collecting small samples in 5 ml syringes and thereafter analysed in the "Paar Stabinger Viscometer SVM 3000".

5.2.1.3 Average oil slick thickness

The recorded videos of the oil slick during the herding experiments were processed by a MatLab code, which converted the time-step frames into a binary code giving black pixels to the area that corresponded to the oil slick. Then the average slick thickness of the oil slick was easily estimated based on the initial poured mass of oil and its density.

5.2.1.4 Burning efficiency

The burning efficiencies, BE is based on the initial oil amount and it is applicable for experiments where oil and emulsions were tested, and it can be calculated by the following expression:

$$BE=100\left(1-\frac{m_f}{m_{0,oil}}\right) \quad (1)$$

Where $m_{0,oil}$ is the mass of the initial amount of crude oil, m_f is the mass of the oil residues left after burning. It is assumed that the water contained in the emulsion evaporates or mixes with the water in the tank during the oil burning.

5.2.1.5 Global mass burning rate

The mass burning rate, \dot{m} , defines the mass lost per unit time of a specimen (crude oil) burning and it is expressed in kg/s or g/s. Herein, the global mass burning rate is studied, because it was not possible to measure the instantaneous weight loss during the experiments owing to the nature of the experimental rig. The global mass burning rate can be calculated by the following equation:

$$\dot{m}_{global} = \frac{m_f - m_{0,oil}}{\Delta t} \quad (2)$$

Where Δt is the time duration of the burning experiment in seconds, $m_{0,oil}$ is the mass of the initial amount of oil and m_f is the mass of the oil residues.

5.2.1.6 Average flame height

The average flame heights were estimated using the same method as van Gelderen et al. (2015). The videos were processed by a script in MatLab that transforms the flame position into a binary code (discrimination of white pixels from the rest) within subsections of 10 seconds. In order to restrict the counting of intermittent flames, the script was conditioned to count only the flame heights that are present at least 60% of the time in each subsection.

5.2.1.6.1 Post-herding (main experiments)

These experiments aimed to study several parameters related to the herder performance and fate, the ignition and burning of the oil slick, and the sample collecting. For this procedure at least triplicates were carried out for each oil/emulsion type in order to ensure good reproducibility. The procedure consisted of 30-minute herding of an oil slick that had already been established on the water surface. After the herding, the oil slick was ignited and burned. The slick was partially confined in order to prevent the slick from moving to the COFA's edges and to enable sampling of the water column underneath the oil slick, but still allow certain drifting and spreading of the oil slick. The partial confinement created some variability in the slick position during the burns, but did not affect the overall outcome significantly. Along with the execution of each experiment the corresponding samples were collected and gathered to be further studied at DCE (see chapters 5.3 and 5.5). Artificial cold saltwater was used with 32 ‰ salinity content and with a temperature between 0-2 °C. The artificial water was prepared by mixing of distilled water and salt without anti-caking agent. A list of the completed experiments is presented in Table 5.

Table 5: Matrix of experiments for post-herding procedure. OP-40 and TS stand for the herders SilTech OP-40 and ThickSlick 6535, respectively.

<i>Oil/emulsion type</i>	<i>Herder type</i>	<i>CODE: Oil_water content_herder</i>	<i>Fuel amount [g]</i>	<i>Number of repetitions</i>
ANS	OP40	ANS_0%_OP40	176	4
	TS	ANS_0%_TS	176	4
Grane	OP40	Grane_0%_OP40	176	3
	TS	Grane_0%_TS	176	3
ANS/25 % water	OP40	ANS_25%_OP40	260	3
	TS	ANS_25%_TS	260	3
Grane/25% water	OP40	Grane_25%_OP40	260	3
	TS	Grane_25%_TS	260	3

The detailed procedure for post-herding experiments was:

1. The water bath surfaces were cleaned thoroughly before each experiment in order to remove possible herder/oil residues from previous experiments.
2. The COFA was filled with 390 litres of cold saltwater, ice cubes were added to obtain the desired temperature.
3. A water sample was taken to measure the water surface tension with a Wilhelmy Plate to verify that the cleaning procedure had effectively removed the herder residues (this was done on a periodic basis with random intervals and the results showed that the cleaning procedure lived up to the requirements every single time).
4. Sampling and measurement equipment was prepared before each experiment: jars for water collection, small vials and sorbent pads for post-burn residues collection, camera for video recording, thermocouples. All doors and windows were closed in order to avoid draft over the COFA.
5. In order to collect samples of any underwater residues either visible or non-visible to the naked eye (to be further analysed at DCE, see chapter 5.3 and 5.6), a Pyrex Glass Cylinder (PGC) was introduced into the centre of the water basin, where it was standing on a steel base that closed it at the bottom end. Then, a 1 litre glass jar was placed within the PGC and another glass jar was placed outside but close to the edge of the PGC. The PGC was immersed in such a way that it would not interfere with the oil slick movement. See Figure 41.
6. The required amount of oil/emulsion was weighed, and poured carefully onto the water surface in the middle of the COFA. The oil was then allowed to spread for 30-45 minutes.
7. The upper camera was set and 150 μl of herder (corresponding to a concentration of 150 $\mu\text{l}/\text{m}^2$) was applied drop-wise around the oil slick at a number of locations with the micropipette and the herder contracted the oil for 30 minutes.
8. The oil slick was confined partially within the PGC edges with a spatula for the purpose of allowing the oil slick to move with certain drift but remain centrally located, thus the

risk of the oil slick moving towards the edges of the water basin was minimized; this task was done with great caution so that the slick was not mixed with water or overly affected. The upper camera box was closed with a cover to protect the camera and a front camera was placed to measure the flame heights.

9. A thermocouple tree was fixed to a holder and placed on the water basin. The cameras were turned on. Thereafter the oil slick was ignited with a butane torch until the fire maintained itself.
10. Video recordings from the upper camera and from the front camera and data from thermocouple tree were stored for later analysis of the oil slick surface and slick thickness and possible flame height. The burn residues were collected with pre-weighed sorbent pads. Containers and jars, were also pre-weighed to be able to calculate the burning efficiency. Several samples were collected for further analysis; these can be grouped as 'before burn' and 'after burn', the samples were collected and properly labelled. A thorough description and visual description of the collected samples can be found in Chapter 5.3.

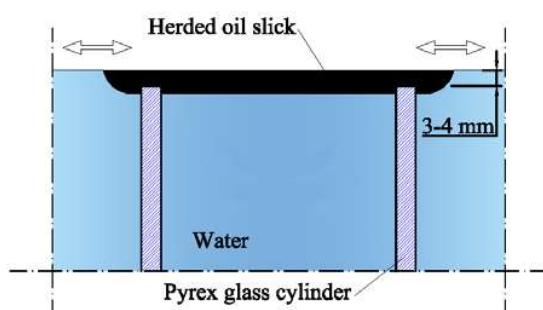


Figure 41: Schematic of the herded oil slick partially confined within the PGC edges

5.2.1.6.2 Pre-herding

The procedure was reversed compared to the previous case, i.e. the herder was applied before the oil. The aim was to study the herding efficiency for a case that can simulate scenarios in the field where oil spills can occur due to a broken pipeline, or for scenarios where the herder could be used to block the oil spill from vulnerable areas such as shorelines, ports, aquifers and other protected marine areas. Furthermore, no samples were taken from the water column underneath the oil slick. Only parameters related to the herding efficiency were studied and no repetitions of the experiment were done. Some of the experiments were executed after the post-herding experiment with the purpose of saving time and resources, this means that in some cases the water temperature was above the pre-established temperature and tap water was used in some cases instead of distilled water. A list of the completed experiments is listed in Table 6.

Table 6: Matrix of planned experiments for pre-herding, long-term and control experiments. OP40 and TS stand for the herders SiITech OP-40 and ThickSlick 6535 respectively.

Type	Oil/emulsion type	Herder type	CODE: Procedure/oil_water content_herder	Fuel amount [g]
PRE-HERDING	ANS	OP40	PH/ANS_0%_OP40	176

	Grane	TS	PH/ANS_0%TS	176	
		OP40	PH/Grane_0%_ OP40	176	
	ANS/25% water	TS	PH/Grane_0%TS	176	
		OP40	PH/ANS_25%_ OP40	260	
	Grane/25% water	TS	PH/ANS_25%TS	260	
		OP40	PH/Grane_25%_ OP40	260	
		ANS	OP40	O/ANS_0%_ OP40	176
			TS	O/ANS_0%TS	176
		Grane	OP40	O/Grane_0%_ OP40	176
			TS	O/Grane_0%TS	176
	ANS/25% water	OP40	O/ANS_25%_ OP40	260	
		TS	O/ANS_25%TS	260	
	Grane/25% water	OP40	O/Grane_25%_ OP40	260	
		TS	O/Grane_25%TS	260	
	ANS	TS	O/ANS_0%TS (2 weeks)	176	
		Grane	TS	O/Grane_0%TS (2 weeks)	176
CONTROL	ANS	None	C/ANS_0%	176	
	Grane		C/Grane_0%	176	
	ANS/25% water		C/ANS_25%	260	
	Grane/25% water		C/Grane_25%	260	

The general procedure for pre-herding experiment was:

1. The water from previous post-herding experiments was cleaned with sorbent pads and reused for this experimental procedure. Otherwise the next steps were completed:
2. The water bath surfaces were cleaned thoroughly before each experiment in order to remove possible herder/oil residues from previous experiments.
3. The COFA was filled up with 390 l of salt water.
4. A water sample was taken to measure the water surface tension with a Wilhelmy Plate in order to verify that the cleaning procedure had effectively removed the herder residues (this was done on a periodic basis with random intervals and the results showed that the cleaning procedure lived up to the requirements every single time). Because no underwater sampling was required, it was not necessary to use the Pyrex Glass Cylinder and jars for these tests.
5. Preparation of upper camera for video recording. All doors and windows were closed in order to avoid draft over the COFA.

6. The upper camera was set and 150 μl of herder was applied drop-wise at a number of locations with the micropipette.
7. The required amount of oil/emulsion was then weighed, and then poured carefully and gently onto the water surface in the middle of the COFA. The oil was then contracted due to the pre-applied herder for 30-45 minutes.
8. Video recordings from the upper camera were stored for later analysis of the oil slick surface.

5.2.1.6.3 Long-term herding

This procedure involved long-run experiments where the duration of the herding ability was studied. The objective for this procedure was to study the herding ability over a long term, because few studies have been reported in the literature for the such a case (Buist et al. 2008). Solely the herding performance was studied in these tests. Contrary to the previous procedures, the water temperature could not be controlled completely during the long-term herding procedure. Therefore, it was chosen to keep the water at room temperature (20 °C) for the duration of each experiment. Furthermore, 4 overnight experiments (up to 20 hours) were performed with salt-water and two last experiments (up to 450 hours) were performed without salt water. A list of the completed experiments is displayed in Table 6.

The general procedure for long-term experiment was:

1. The water bath surfaces were cleaned thoroughly before each experiment in order to remove possible herder/oil residues from previous experiments.
2. The COFA was filled up with 390 l of salt water or with tap water, depending on the experiment, see above.
3. A water sample was taken to measure the water surface tension with a Wilhelmy Plate in order to verify that the cleaning procedure had effectively removed the herder residues (this was done on a periodic basis with random intervals and the results showed that the cleaning procedure lived up to the requirements every single time.)
4. Preparation of measurements were carried out before each experiment: camera for video recording and lamp for illumination of the COFA during night time to avoid very dark corners
5. The required amount of oil/emulsion was then weighed, before it was poured water surface.
6. The upper camera was set to take either videos or pictures every 30 minutes and 150 μl of herder was applied drop-wise at a number of locations with the micropipette.
7. Video recordings from the upper camera were stored for later analysis of the oil slick surface.

5.2.1.6.4 Control (main experiments)

The experiments following this procedure were to give reference results, related to the burning of the oil slick, to be compared against results obtained during the "post-herding" combustion experiments. No herding agents were used, so there was no need to use salt water. Instead, the oil slick was completely confined in a Pyrex glass cylinder and regular cold tap water was used. The oil slick thickness for Grane, ANS and their corresponding water-in-oil emulsions ranged from 3.5 to 4mm. A list of the completed experiments is listed in Table 6.

The general procedure for control experiment was:

1. The water bath surfaces were cleaned thoroughly before each experiment in order to remove possible herder/oil residues from previous experiments.
2. The COFA was filled up with 390 l of cold tap water.
3. A water sample was taken to measure the water surface tension with a Wilhelmy Plate in order to verify that the cleaning procedure had effectively removed the herder residues (this was done on a periodic basis with random intervals and the results showed that the cleaning procedure lived up to the requirements every single time.)
4. Preparation of measurements, were prepared before each experiment: sorbent pads for post-burn residues collection, camera for video recording, thermocouples. All doors and windows were closed in order to avoid draft over the COFA.
5. A Pyrex Glass Cylinder (PGC) was introduced into the water basin centrally, which was placed onto a closed steel foot. The required amount of oil or emulsion was then weighed, and then poured within the edges of the PGC, thus it ended totally confined. See also Figure 42.
6. The thermocouple tree was fixed to a holder
7. The upper camera and frontal camera were set; thereafter the oil slick was ignited with a butane torch until the fire is maintained by itself.
8. Video recordings from the upper camera and from the front camera and data from thermocouple tree were stored for later analysis of the oil slick surface and slick thickness and possible flame height.

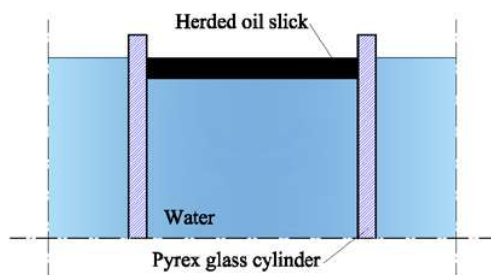


Figure 42: Schematic overview of the herded oil slick totally confined within the PGC edges.

5.2.2 Results

The overall results are presented in the following subchapters, which comprise the results concerning the herding efficiency and the parameters related to in-situ burning for the main experiments or "post-herding". Results from additional experiments that were conducted in order to increase the understanding of the herder efficiency and duration and the burning mechanism are also reported: these are pre-herding, long-term and control experiments. Furthermore, the slick thickness results are compared between post-herding and pre-herding procedures. The burning efficiencies, global mass burning rate, and flame height results from the post-herding procedure are compared to their counterpart-parameters from the control procedure. A detailed representation of the results by procedure and comparison can be seen in Figure 43. Whenever possible, the obtained results were compared against other results from similar studies in order to validate the method.

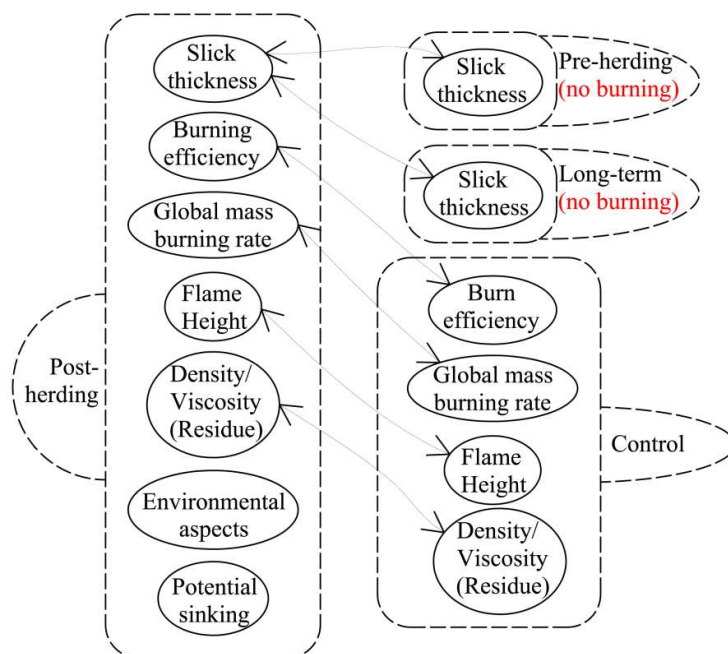


Figure 43: Overview of results according to their procedure type and comparison of results.

5.2.2.1 Burning efficiency

A summary of results concerning the burning efficiencies of all the experiment runs are displayed in Table 7. The burn efficiencies are listed; BE is estimated based solely on the initial oil mass for both experiments with crude oils or water-in-oil emulsions, in the latter the water content is not considered.

The burning efficiencies achieved in the experiments at DTU are as expected for low oil amounts. It is worth mentioning that there are some essential differences in the methods that were used at DTU and SL Ross. In the latter, the confinement of the oil slick within a metal rig and the high suction rate and the proximity of the ventilation system are factors that influence the combustion process. As such, it is only expected that there is a variation between the experiments in the two labs should not cause any concern. First, radiative feedback is expected from the metal ring. Second, larger convective flows (chimney effect) are expected due to the high velocity and the proximity of the ventilation system. At DTU (see Fig. 40), no metal ring was used and the ventilation system was not in the proximity (it was placed 1.8 m. above the oil slick). Furthermore, there is a clear correlation between the size of the oil amount and the burning efficiency. For smaller oil amounts, lower burning efficiencies are achieved, and for much larger oil amounts, higher burning efficiencies are achieved, as can be seen in Figure 46.

As seen, the average burning efficiency result for ANS crude oil, 37%, is higher than Grane's 26% and 21% burning efficiencies in the current experimental set-up. This is somehow an expected behaviour owing to the difference in properties for the oils. ANS is a medium grade crude oil with a lower density and viscosities than Grane, which is a much more viscous and asphaltenic crude oil. ANS has more light components (short hydrocarbons) than Grane, and therefore a higher burning efficiency is achieved by ANS. It was also observed during the experiments that Grane was more difficult to ignite than ANS owing to its higher fire point and flashpoint.

Table 7: Summary of burning efficiencies results for both crude oil and their corresponding emulsions.

Oil type	Experiment code <i>Oil_water content_herder type/oil weight/trial number</i>	Water content [%]	Herder Type	BE [%] ¹⁾	Average BE [%]
ANS	ANS_0%_OP40/176/1	0	OP40	34	37 ± 3
	ANS_0%_OP40/176/2			39	
	ANS_0%_OP40/176/3			39	
	ANS_0%_OP40/176/4			35	
	ANS_0%_TS/176/1	0	TS	31	37 ± 5
	ANS_0%_TS/176/2			39	
	ANS_0%_TS/176/3			38	
	ANS_0%_TS/176/4			40	
	ANS_25%_OP40/215/1	25	OP40	51	49 ± 7
	ANS_25%_OP40/260/2			55	
	ANS_25%_OP40/260/3			41	
	ANS_25%_TS/260/1	25	TS	53	55 ± 2
ANS_25%_TS/260/2	55				
ANS_25%_TS/260/3	56				
Grane	Grane_0%_OP40/176/1	0	OP40	33	26 ± 5
	Grane_0%_OP40/176/2			21	
	Grane_0%_OP40/176/4			24	
	Grane_0%_TS/176/2	0	TS	25	21 ± 4
	Grane_0%_TS/176/3			17	
	Grane_0%_TS/176/5			21	
	Grane_25%_OP40/260/2	25	OP40	37	39 ± 3
	Grane_25%_OP40/260/3			38	
	Grane_25%_OP40/260/4			43	
	Grane_25%_TS/260/1	25	TS	39	48 ± 8
	Grane_25%_TS/260/4			48	
	Grane_25%_TS/260/5			58	

¹⁾It should be noted that burning efficiencies in smaller, lab-scale experiments like this (oil spill diameter of 26 cm) are known to produce lower Burning Efficiencies than large scale experiments, and the BEs should therefore only be used for comparison between and understanding of the current experiments. See also Figure 46.

The burning efficiencies for ANS and Grane 25% water-in-oil emulsions, 49-55% and 39-48%, respectively, are higher than those for fresh ANS and Grane, which were 37% and 21-26%, respectively. The burning mechanism of emulsified oil differs greatly from fresh crude oils burning

under same conditions. Higher temperature is required to break down the emulsion in order to boil the water off, above 100 °C (Brandvik et al. 2010), so the small water droplets can evaporate and thus form a layer of pure oil on top of an emulsion layer. It has been reported that the water content in emulsified oils increases the fire point (Buist et al. 2013). Also, at some point the temperature of the emulsified oil layer increased due to the heat transfer from the oil burning layer, which is able to boil off all or a part of the encapsulated water droplets. As a result, this can trigger a violent boilover at the end of the burning process (Buist and Glover 1995), producing a sharp increase in the flame height (Potter and Buist 2008). For the Grane crude oil, slightly lower burning efficiencies were achieved by TS than OP40. Otherwise, at small-size and for these experiments and method, it seems that there is not large difference in burning efficiency using OP40 or TS.

The data concerning average burning efficiencies for both crude oils and 25% water-in-oil emulsions are displayed in Figure 44 and Figure 45, where the results from the control experiments are displayed as well.

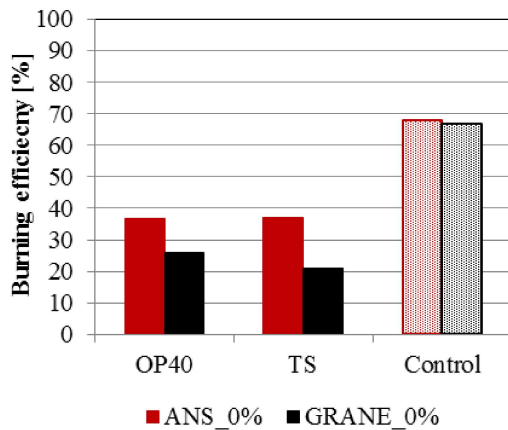


Figure 44: Average burning efficiency results for ANS and Grane crude oils from post-herding experiments and control experiments. Note It should be noted that burning efficiencies in smaller, lab-scale experiments like this (oil spill diameter of 26 cm) are known to produce lower Burning Efficiencies than large scale experiments, and the BEs should therefore only be used for comparison between and understanding of the current experiments. See also Figure 46.

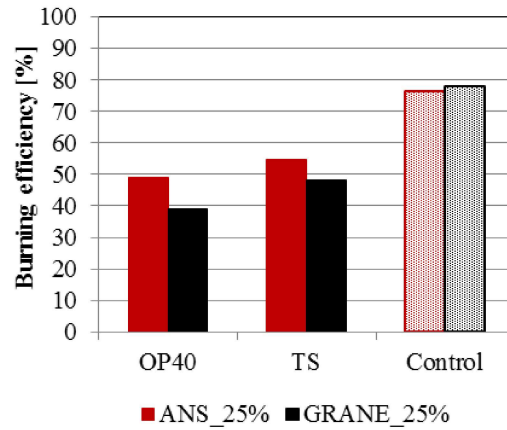


Figure 45: Average burning efficiency results for ANS and Grane 25% water-in-oil emulsions from post-herding experiments and control experiments. Note It should be noted that burning efficiencies in smaller, lab-scale experiments like this (oil spill diameter of 26 cm) are known to produce lower Burning Efficiencies than large scale experiments, and the BEs should therefore only be used for comparison between and understanding of the current experiments. See also Figure 46.

There is a noticeable difference between the average burning efficiencies results from both crude oils ranging between 21% and 37% and the burning efficiencies from the control experiments, which are 67% and 68% (Burning efficiencies based only on the initial oil amount, BE). In the control experiments, the oil slick was fully confined within the pyrex glass cylinder and the thickness of Grane and ANS ranged from 3.5 to 4 mm.

The large difference in burning efficiency, for these experiments, can be explained by the fact that a fully confined oil slick reaches higher temperatures and there is less heat transfer towards the water level since the oil slick thickness varies depending on the mass burning rate. As a result,

the area of the slick remains constant through the combustion. In comparison, during the burning in post-herding experiments, the oil slick area increased, resulting in a decrease in the oil slick thickness since it spread once it was ignited, and thus a greater contribution to the heat transfer to the water. This spreading phenomenon might explain why the burn efficiencies results from both herded oils, are significantly lower than those obtained in Sub-Chapter 4.2.2.4. It seems that the spreading would affect the burning efficiency of smaller oil slicks more than bigger oil slicks. Nonetheless, with large oil amounts, it is likely that the oil slick does not expand during combustion due to the flames producing large convective radial flows that also help to thicken the oil slick along with the herding agent.

Furthermore, during the control experiments, higher boilover tendencies were observed with significantly increased flame heights. This phenomenon contributed greatly to the increased burning efficiency.

The burning efficiencies for the control experiments with the 25% water-in-oil emulsions are even higher, in the range 76-78 %. In addition to the combustion contribution from the boiling of small water droplets, the confinement contributes to higher burning efficiency in these experiments as well.

The stability of the emulsion is one of the factors that defines its ignitability (Brandvik et al. 2010). Stable emulsion with 25% water content or higher are not ignitable, but meso-stable with higher water content can be burned (Buist and Glover 1995; Buist et al. 2013). Furthermore based on laboratory work by SL Ross, ANS will not form a stable emulsion, and work by SINTEF shows that Grane will form a stable emulsion (see Chapter 4). For the current study, the measured viscosities for both emulsified oils were twice as much as that of the initial oil. It is clear that the emulsions' preparation technique and the type of oil affect the stability of the water-in-oil emulsion and thus the results in terms of burning efficiency.

In general, relatively low burn efficiencies were achieved for most of the experiments, ranging between 21-37% and 39-55% for both crude oils and their corresponding 25% water-in-oil emulsions, respectively. The rather low burning efficiencies are most likely due to the relative small size of the experiments. Herein, small amounts of oil were tested, namely 170 g and 250 g for both crude oils and their corresponding 25% water-in-oil emulsions, respectively.

Overall, the burning efficiency results are somewhat in the same range as results reported in the literature. In Figure 46 the current burning efficiencies of the ANS and Grane crude oils are displayed together with results reported in previous studies. The data is displayed within two Regimes, I and II. Buist et al. (2008) performed small-scale experiments in wind/wave tanks with ANS crude oil and the TS herding agent (formerly known as USN) under open water and drifting conditions, obtaining burning efficiencies in the range 40-59% for oil amounts in the order of 180-360 g. In another study, Buist & Meyer (Buist and Meyer 2012) carried out small-scale burn tests in a wind/wave tank and reported burning efficiencies in the range 36-50% for oil amounts of 350 g approximately. These results are in accordance with the current results for ANS, something which indicates that the current methodology and experimental set-up is appropriate. Furthermore, the reproducibility of the results was good and within $\pm 10\%$ variation in burning efficiency. From Figure 46 it can be seen that the larger the amount of tested oil, the higher the burning efficiency. Buist et al. (2011) performed mid-scale experiments at Prudhoe bay in Alaska with ANS crude oil and TS herding agent, they reported burning efficiencies of 38 % and 70 % for 6 kg and 13 kg of oil, respectively. In another study, they (Buist et al. 2011, 2013) performed large-scale burning experiments in the Barents sea, just off Svalbard-Norway, and reported burning

efficiencies of 80 % and 94 % for 102 and 630 L of Heidrun crude oil, respectively. The herding agent in these experiments was also TS. Several in-situ burning experiments were performed for ANS in ice cavities by Rangwala et al. (Rangwala et al. 2013) where the diameters of the ice cavity pools were 5, 36 and 128 cm.

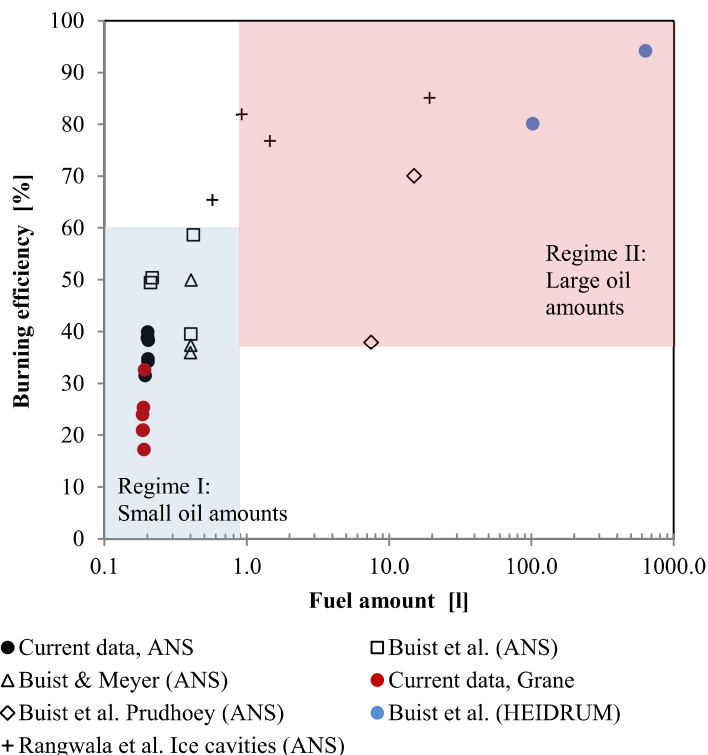


Figure 46: Comparison of the current burning efficiency results with results from similar studies. Only results from fresh crude oils are displayed.

First, the contrast between small results within the “Regime I” is explained by the difference between methods used for the several small-scale experiments. In some cases, the particular set-up might have contributed to the combustion process, and hence relatively larger burning efficiencies were achieved. Also, for data points lower than <40%, less convective radial flow was achieved and the oil slick therefore expanded, which affects the burning efficiency in a negative manner. Thus, the experimental set-up has a large impact on the results for small-scale experiments.

Second, even there are many non-controlled variables and different experimental procedure from the large-scale experiments. In Figure 46, the contrast between small-scale data and large-scale data might indicate that for larger amounts of oil, more energy and more convective and radiative heat is generated, thus larger amounts of oil are burned, specially, radiative heat dominates in large pools (Hurley et al. 2016). And the spreading of the ignited hot oil has a smaller overall effect as the fire size increases due to the larger radial convective flows produced by the flames.

Even though this is a known fact for decades, there is not such a “correlation” or “tool” that could indicate how successful a large-scale in-situ burning would be, based on small or middle scale experimental data, to the knowledge of the authors. Notice that the data in Figure 46 correlates to a certain degree, this is an attempt to establish a correlation between small and large scale

experiment. However, more full-scale and mid-scale data with other crude oils and emulsified oils is required to properly further conclude that the fuel amount will indeed be the main parameter for the burning efficiency.

5.2.2.2 Herding efficiency

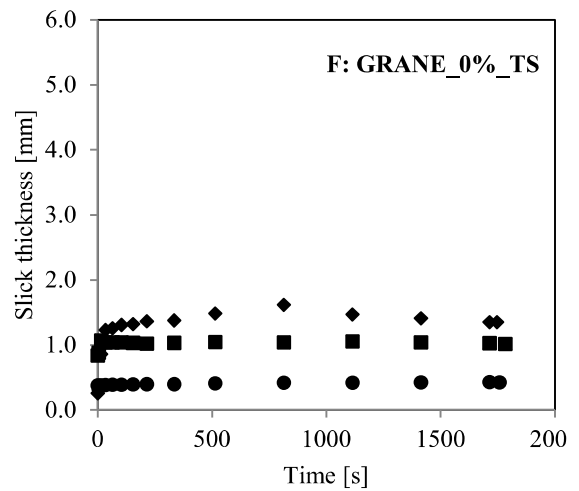
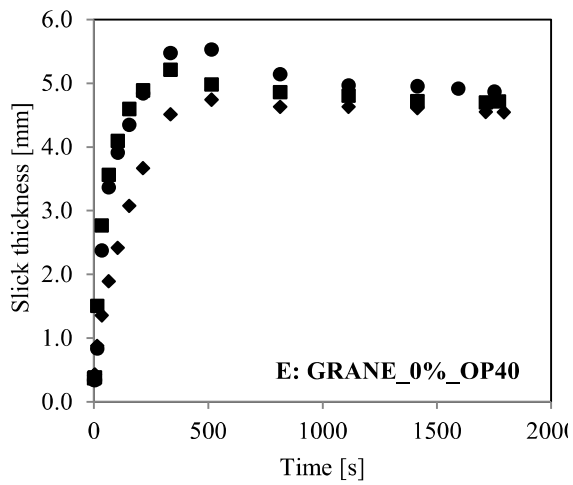
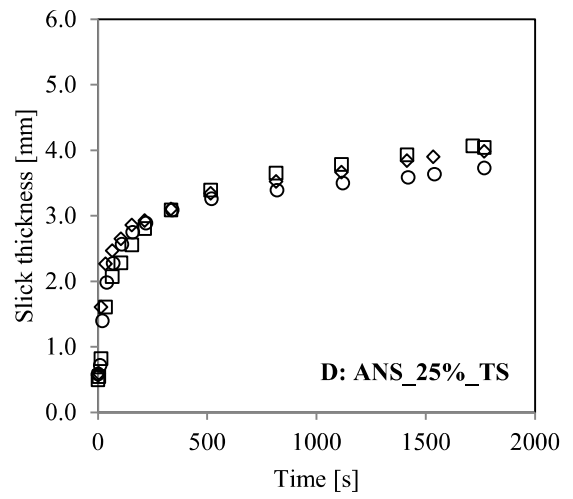
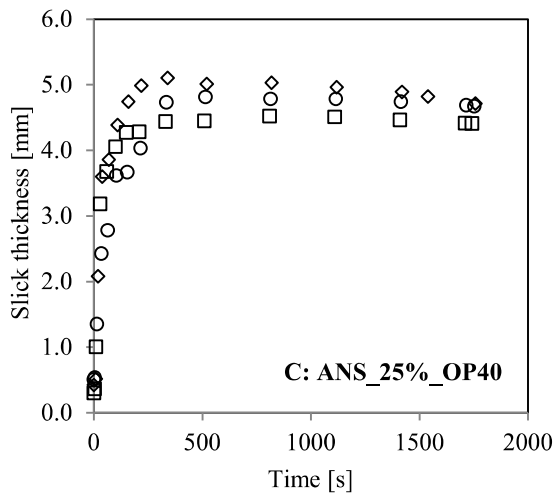
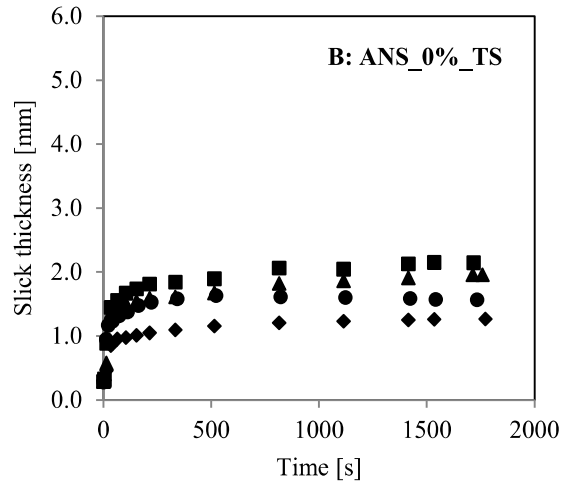
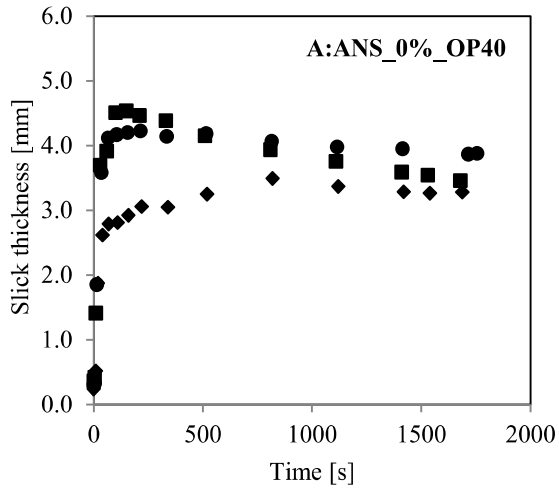
5.2.2.2.1 Post-herding (main experiments)

The herding of ANS crude oil with OP40 and TS achieved slick thickness with significant differences, see Figure 47 (A-B). The OP40 thickens the oil slick significantly within the first minute, and then the oil slick thickness tended to decrease slightly until the slick seemed to follow a steady behaviour. The average oil slick thickness achieved by OP40 was much larger than those achieved by TS. Furthermore, TS thickened the oil slick at a slower pace than OP40 initially, and after the first minutes the oil slick thickness did not vary. This asymptotic behaviour was observed until 30 minutes had passed.

The herding of ANS 25 % water-in-oil emulsion with OP40 shows a similar behaviour as with fresh ANS, but after the initial increase in thickness, there is a more stable behaviour; see Figure 47 (C). Also, the obtained thicknesses with ANS 25 % water-in-oil emulsion with OP40 are greater than with ANS crude oil. The other herder, TS, showed a different, non-asymptotic, behaviour as it continued thickening the oil slick up to 30 minutes, see Figure 47 (D). The obtained thicknesses for the ANS 25 % water-in-oil emulsion with TS are much greater than those obtained with the fresh ANS.

When herding the Grane crude oil, both herding agents showed the same efficiency differences as with ANS, i.e. OP40 was faster in the beginning and obtained thicker oil slicks than the TS, see Figure 45 (E-F). Nonetheless, the herding agent OP40 achieved thicker oil slicks with Grane than with ANS, whereas the opposite was found for TS, see Figure 47 (F). The thickening of Grane 25% water-in-oil emulsion with OP40 occurred at a much slower pace in the beginning and achieved thinner slick thicknesses than in the previous cases, see Figure 47 (G). A poor, but slightly better performance by the TS herding agent was observed in the Grane 25 % water-in-oil emulsion as compared to fresh Grane, see Figure 47 (H).

In summary, the OP40 herding agent performed better with Grane than with ANS, but the opposite trend was observed for the water-in-oil emulsions. This is in agreement with other studies where it has been demonstrated that the silicon-based herding agents (OP40 and others) outperform the hydrocarbon-based ThickSlick 6535 herding agent (Buist et al. 2011, 2013; Buist, Canevari, and Nedwed 2009; Buist, Potter, and Belore 2010). In general, it was observed that the OP40 thickened the oil slick within the first minutes. The TS showed lower performance compared to OP40. Nevertheless, the ANS water-in-oil emulsion was thickened with similar thickness as those achieved by OP40.



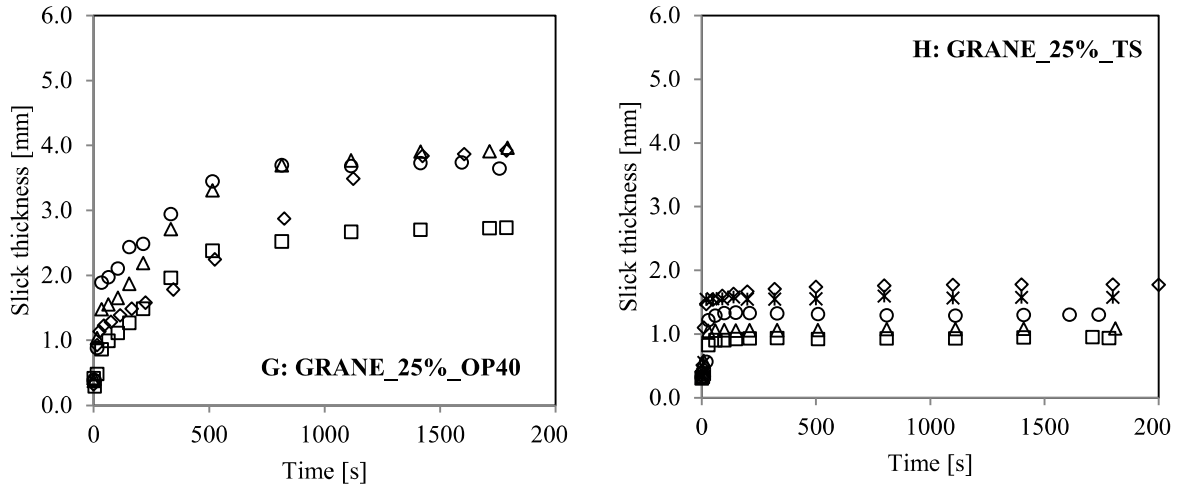


Figure 47: Average slick thickness as function the time. Several replicate runs for ANS and Grane and emulsified oils herded with OP40 or TS, respectively.

The thicknesses achieved by the TS herding agent for both crude oils were rather thin and differs from previously reported results, where it has been found that thicknesses in excess of 3 mm were routinely achieved, even after 30 minutes (At least, this is the case for ANS crude oil herded with TS or formerly called USN) (Buist and Meyer 2012; Buist et al. 2008, 2011). This large contrast in behaviour might be due to differences in the experimental procedures and possibly due to sheen formation for the Grane crude oil. According to Buist et al. (Buist et al. 2011), sheens formed around the oil slick might have different surface tension than the main oil slick. In addition, the poor performance of TS was also observed during tests at CRREL. This could be explained by other two possibilities: either the ANS crude is different than earlier samples, or the batch of TS was not properly formulated or blended (See Chapter 4).

5.2.2.2.2 Pre-herding experiments

In Figure 48, the pre-herding experiment results for both herding agents on ANS and Grane crude oils and their respective 25% water-in-oil emulsions are displayed. Thick oil slick thickness were achieved in the beginning, especially for Grane, followed by a slightly decrease (right pane Figure 48). ANS 25% water-in-oil emulsion herded with TS showed a slight increase in thickness at the end (left pane in Figure 48).

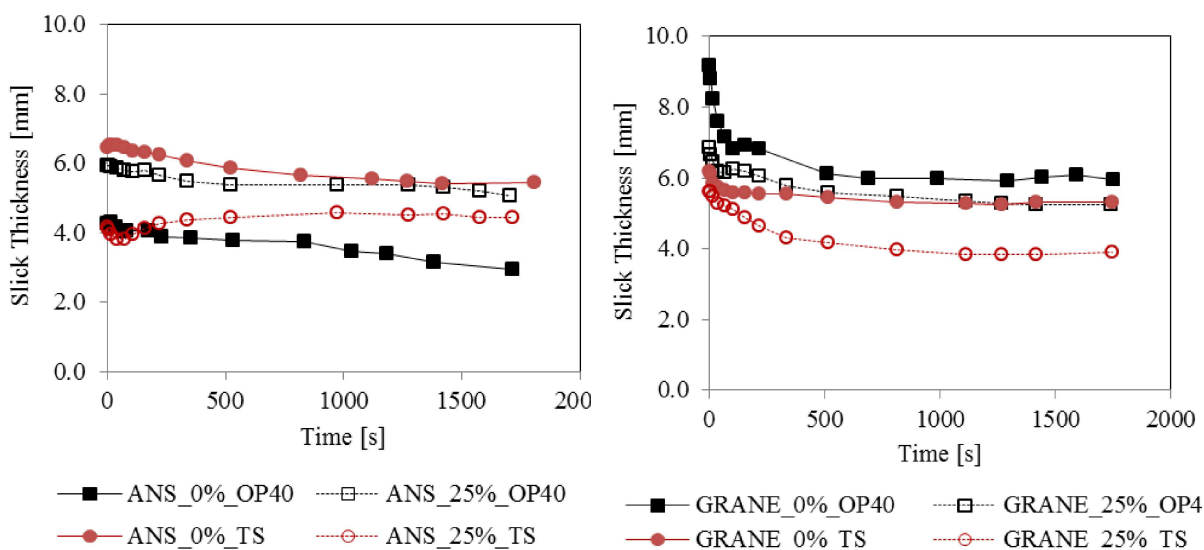


Figure 48: Average slick thickness as function of time. Results from the pre-herding experiments for both crude oils and their respective water-in-oil emulsions herded with OP40 and TS.

The TS achieved greater oil slick thickness than OP40 on ANS crude oil, whereas OP40 achieved thicker oil slick thicknesses than TS for Grane crude oil and ANS and Grane 25% water-in-oil emulsion. These slick thicknesses achieved during pre-herding are much thicker than those achieved during the post-herding experiments. This could be explained by the fact that there is an increase contact surface between the crude oil and the monolayer created by the herder.

5.2.2.2.3 Long-term experiments

The results for the OP40 and TS herding agents on both crude oils and their corresponding 25% water-in-oil emulsions can be seen in Figure 49 for 20 hours herding ability duration studies. It was assumed that the evaporative losses had minor or negligible effect on the measured oil slick thickness.

Three phases can be described from the displayed results on the left graph regarding the OP40 herding agent. First, the peak-phase that lasted 45-60 minutes. Within this period the maximum slick thickness was achieved by the OP40 herding agent for both crude oils and their corresponding 25% water-in-oil emulsions. Second, the decay-phase where the herding efficiency of OP40 followed a stagnation within the next 3-4 hours, and third, the inert-phase, which lasted 1-6 hours, where the oil slick thicknesses almost returned to the original conditions. It is not clear whether the OP40 potentially evaporated or dissolved and dispersed (See Chapter 5.3), or the herder's monolayer dissolved at the edge of the oil slick.

On the contrary, a completely different behaviour can be seen in the right plot, where the TS herding agent thickened both crude oils and emulsified oils within the first minutes. Then, a steady behaviour was observed throughout the duration of the experiment where the oil slick is no further thickened. Note that the TS herding ability did not diminish, i.e. there was no decrease of the oil slick thickness even for these long-duration studies (20 hours).

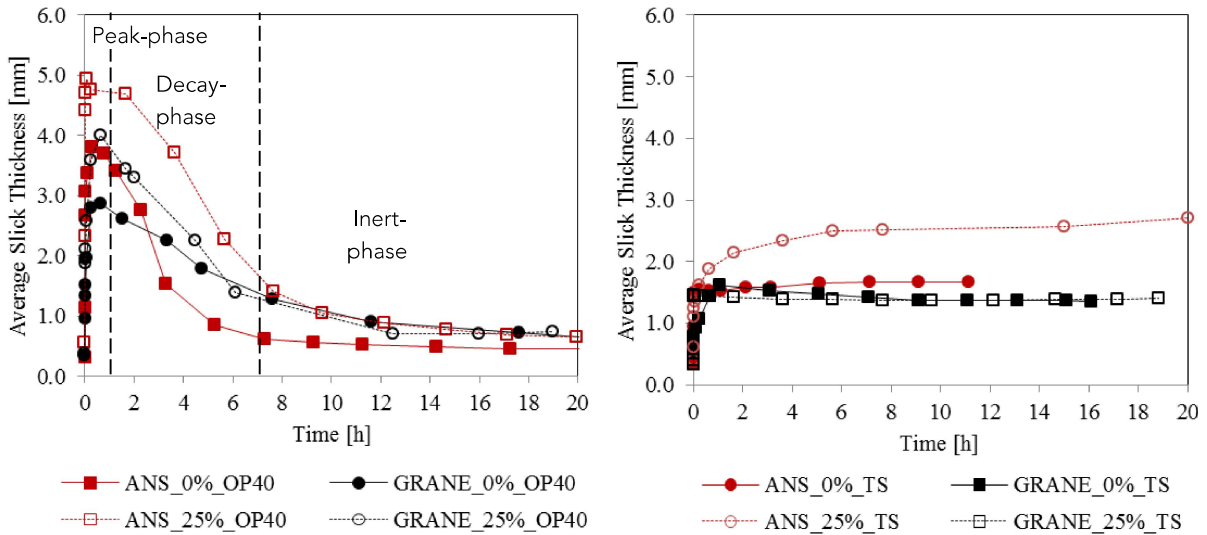


Figure 49: Average slick thickness as function of time. Results from the long-term experiments for both crude oil and their corresponding 25% water-in-oil emulsions herded with OP40 (left graph) and TS (right graph).

Based on the previous results with TS herding agent, two extra experiments with a longer duration (up to three weeks) were completed in order to investigate the stagnation phase of the TS herding agent on both crude oils. The results are displayed in Figure 50, where it can be seen that the herding agent TS achieved maximum thickness with Grane after 20 hours approximately, and with ANS crude oil the maximum thickness was obtained after 50 hours. The ANS oil slick started a rapid decay phase after 5 days, at a pace of $69 \cdot 10^{-3} \text{mm/h}$. On the contrary Grane had two much slower oil slick thickness decreasing phases. The first started after 20 hours, at a pace of $10 \cdot 10^{-3} \text{mm/h}$ and the second started after 350 hour at a pace of $34 \cdot 10^{-3} \text{mm/h}$. These results show that TS herding efficiency had a very low decline, and that the oil slicks for the crude oils started to decay in thickness at very different times at paces. This different behaviour could be due to differences in the evaporative losses for the two crude oils (ANS being most easily evaporated) which might have contributed to a change in surface tension for both crude oils. Also the potential of dissolution/dispersion of the monolayer into the edge of the oil slick could occur differently with different oil types.

Nonetheless, the oil thickness achieved for both crude oils presents an opposite behaviour, as seen in Figure 47. During the first 45 minutes, the thicknesses achieved by ANS and Grane were around 3 mm and 5 mm, respectively. The main difference between these two long-term experiments and the post-herding experiments relies on the water temperature and salt content, 20 °C versus 0-2 °C.

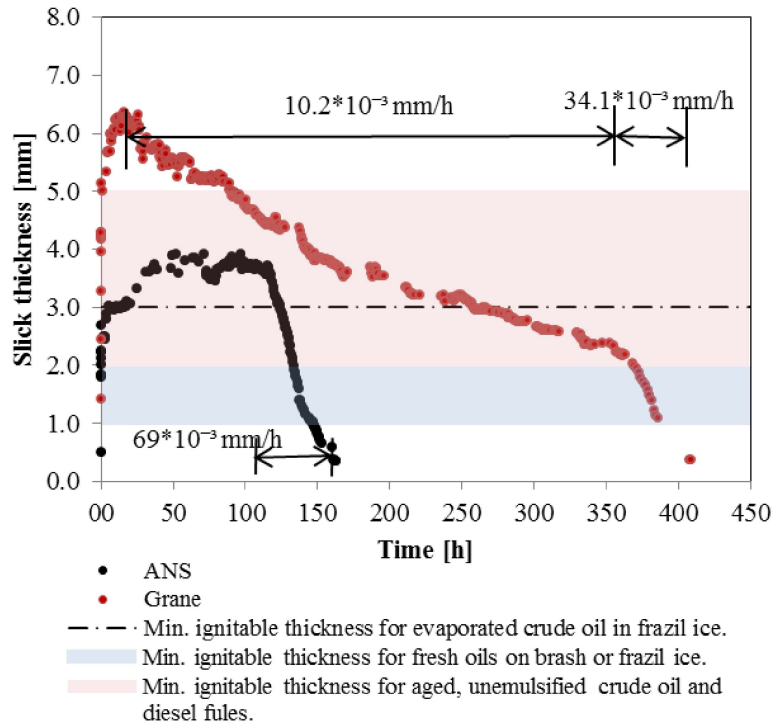


Figure 50: Average slick thickness as a function of time. Results from long-term experiments with both crude oils herded with TS, and minimum ignitable thickness for crude oil under several scenarios (Buist et al. 2013; Fritt-rasmussen 2010; Potter and Buist 2008).

5.2.2.3 Herding fate during and after burning

Based on visual observation from the video recordings (see Figure 51), both herding agents were able to re-thicken the oil slicks even after the flames had extinguished. As can be seen, the oil slick expanded and moved during burning. Most likely, the heat transfer changes the surface and interfacial tension between the oil and the water significantly. Additionally, the oil slick area was estimated during and after the execution of the experiments, see Figure 52 and Figure 53. No significant difference in thickening efficiency was observed for both herding agents once the flames were extinguished.

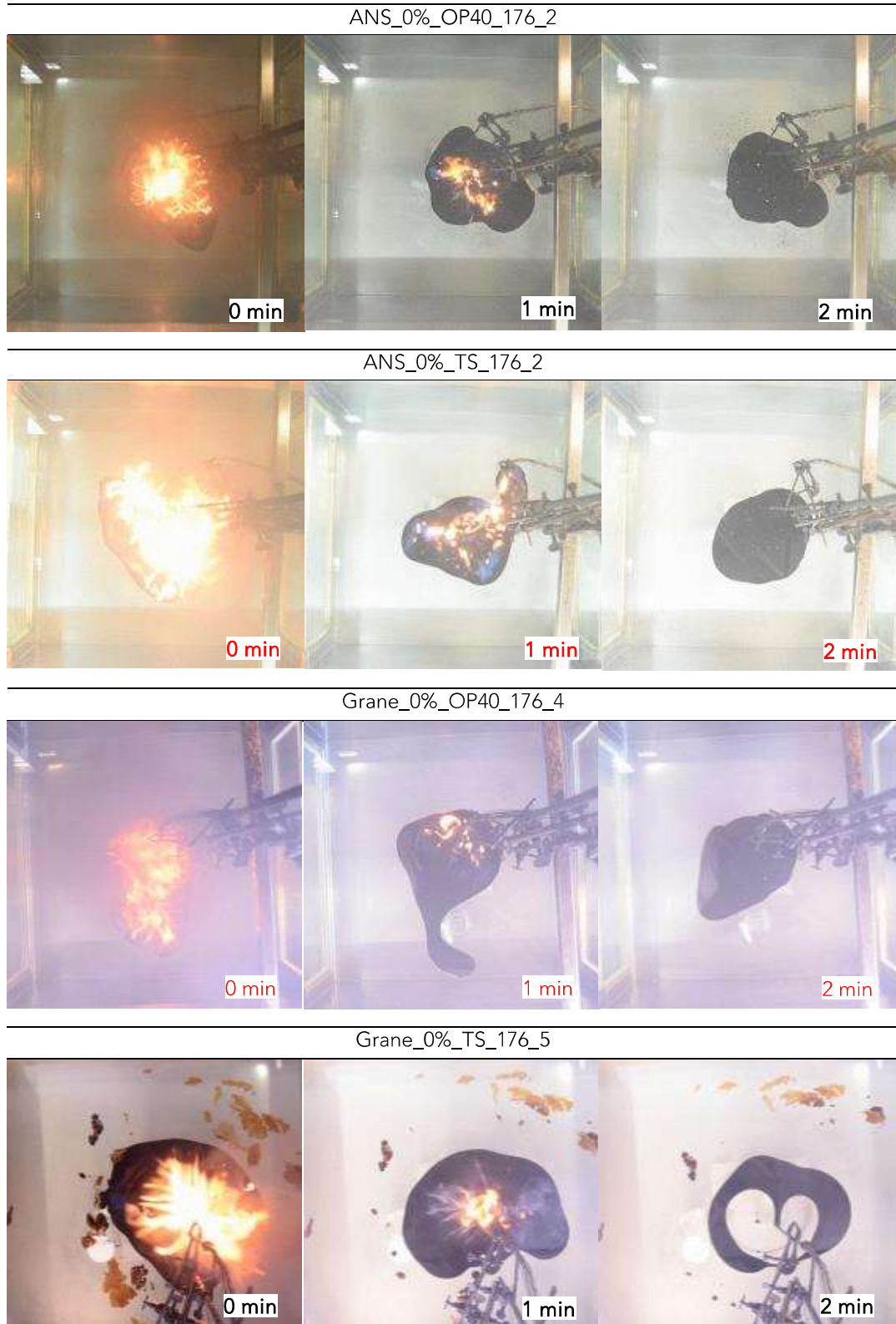


Figure 51: Visual sequence of herding efficiency from both herding agents during burning of the herded ANS and Grane oil slicks and after the flames extinguished.

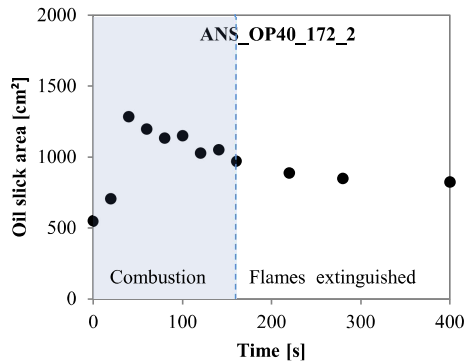


Figure 52: Oil slick area during and after burning for ANS crude oil herded with OP40.

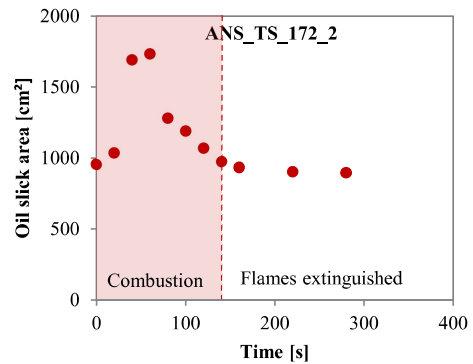


Figure 53: Oil slick area during and after burning for ANS crude oil herded with TS.

5.2.2.4 Global mass burning rate

The average results of several experiments for the global mass burning rate are displayed in Figure 54 where it can be seen that more ANS crude oil is burned per unit time than Grane, which again, can be explained by their differences in physical properties. This observation also applies for the 25% water-in-oil emulsions. The emulsified oils have higher global mass burning rates than both crude oils. This is related to results for the burning efficiencies and again the mechanisms of the emulsified oil play a certain role. Finally, the results from the control experiments are greater than those from the herding experiments, which suggests that the totally confinement of the oil slick is more efficient than burning of the oil confined with herders, at least for small scale experiments.

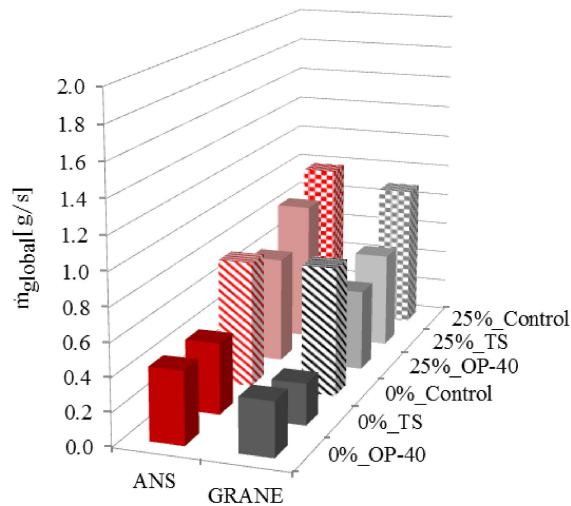


Figure 54: Average global mass burning rate results for both crude oils and their corresponding emulsions from post-herding procedure experiments. Results from control experiments are displayed as well.

5.2.2.5 Viscosities and densities

After each experiment for the crude oils and their emulsions, the viscosities of the oil residues were measured, and the results for ANS and ANS 25% water-in-oil emulsion as a function of the burning efficiency (BE) can be seen in Figure 55 and Figure 56, respectively. The data appear to

correlate, although with some scattering. This might be due to the nature of the experiment. Further experiments are required in order to fully verify the observed trend.

Figure 57 shows the results for the density, and two groups of data-points can be identified: one for the crude oil and the other for the emulsified oil. This observation is not consistent, as it was expected that the density would increase for large burn efficiencies. This anomaly can be contributed to the non-uniform burning of the oil, but further experiments with emulsions should be carried out to confirm this.

The quantitative quality of these results is unclear, but they are included for comprehensive presentation of all the measurements taken during these experiments.

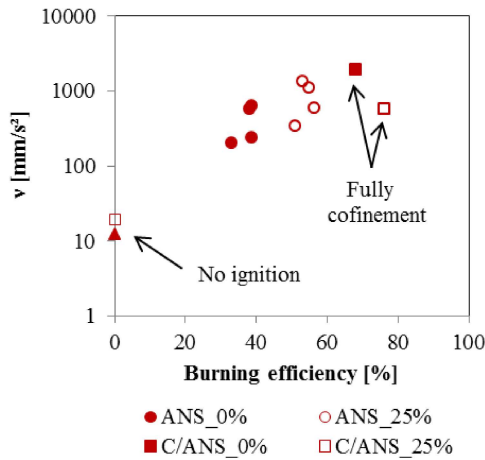


Figure 55: Kinematic viscosity of the oil as a function of the burning efficiency. Results from the experiments with ANS crude oil and its corresponding emulsion.

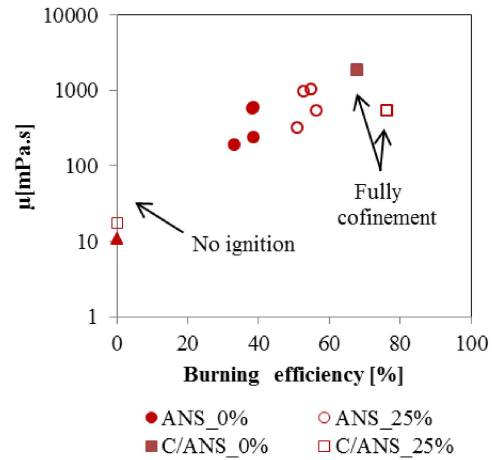


Figure 56: Dynamic viscosity of the oil as a function of the burning efficiency. Results from the experiments with ANS crude oil and its corresponding emulsion.

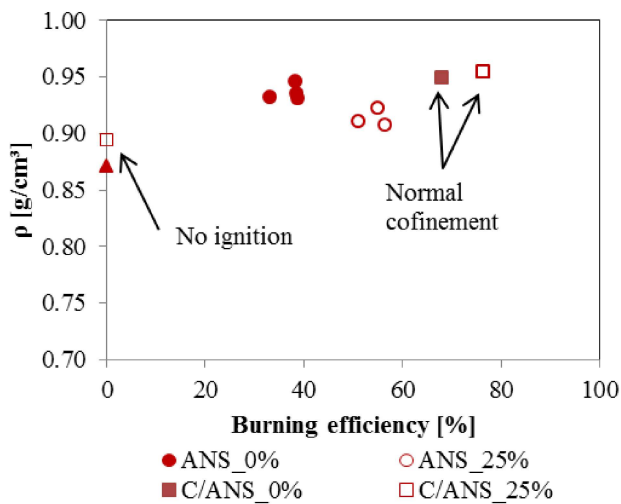


Figure 57: Density of the oil as a function of the burning efficiency. Results from the experiments with ANS crude oil and its corresponding emulsion.

The viscosity as a function of burning efficiency for Grane and Grane 25% water-in-oil emulsion can be seen in Figure 58 and Figure 59. It is quite perceptible that there is correlation for the viscosities. This fact might suggest that the Grane oil in general burns more uniformly than ANS. The data also suggest that for low burning efficiencies, the viscosities increases exponentially, followed by a steady phase between 40% and 60% burning efficiencies.

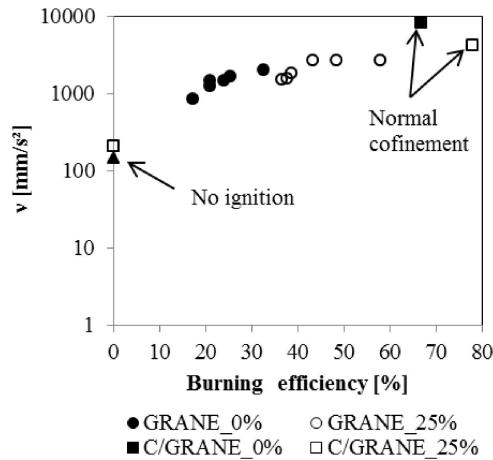


Figure 58: Kinematic viscosity of the oil as a function of the burning efficiency. Results from the experiments with Grane crude oil and its corresponding emulsion.

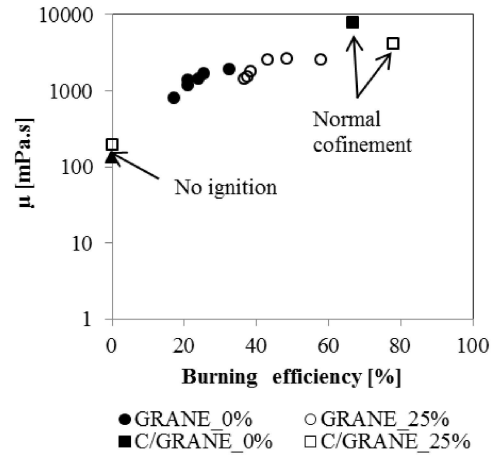


Figure 59: Dynamic viscosity of the oil as a function of the burning efficiency. Results from the experiments with Grane crude oil and its corresponding emulsion.

Figure 60 shows the density results for Grane, and the data again suggest a trend. However, some of the data lies rather scattered, suggesting that the burning was non-uniform to some extent. Also, it seems that there was a steady phase for a range between 40-70%, but more data is required to validate this.

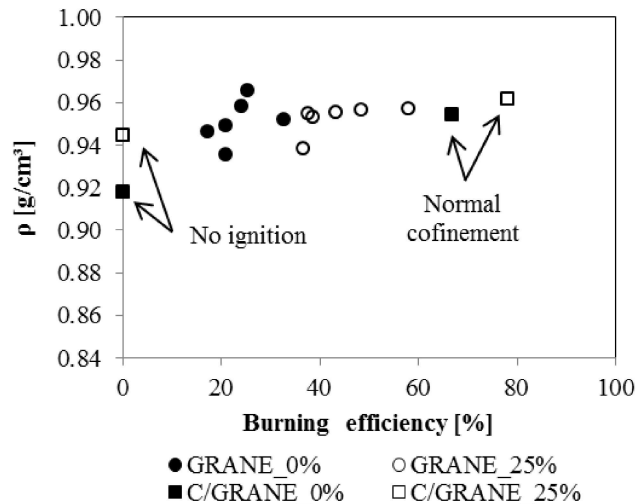


Figure 60: Density of the oil as a function of the burning efficiency. Results from the experiments with Grane crude oil and its corresponding emulsion.

5.2.2.6 Flame heights

5.2.2.6.1 Main experiments

The results for the average flame heights as a function of time for ANS and its 25% water-in-oil emulsion are displayed in Figure 61 and Figure 62, respectively. It can be seen that there is a difference regarding the flame heights results between several experiments for fresh ANS, specially for the 3rd run. This is presumably due to the influence of the partially confinement of the oil slick and the oil slick expansion during combustion, see Figure 61. These results are lower when compared to the average flame heights results obtained for the emulsified ANS oils, see Figure 62, it was observed during the burning of the emulsified oil slick that more intense and violent boilover occurred, prompting peaks in the flame heights. This was followed by flame extinction. This behaviour resulted in higher burning efficiency for the emulsified ANS, as mentioned in Sub-Chapter 5.2.2.1.

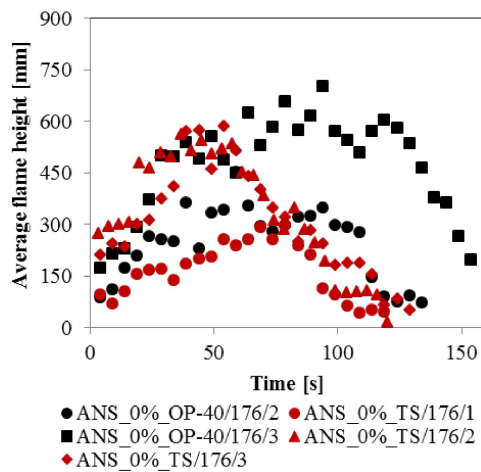


Figure 61: Average flame heights results as a function of time for ANS crude oil herded with OP40 and TS. Several experimental runs from Post-herding procedure.

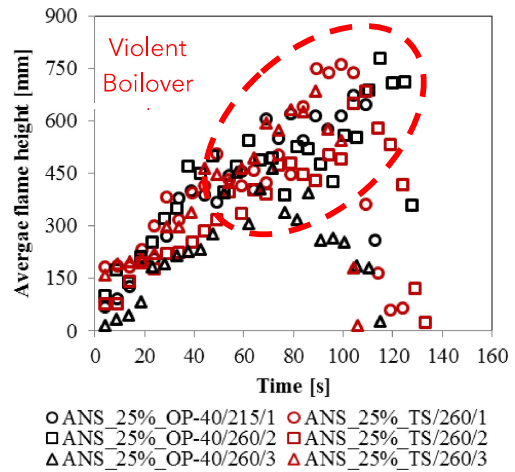


Figure 62: Average flame heights results as a function of time for emulsified ANS oil herded with OP40 and TS. Several experimental runs from Post-herding procedure.

The average flame heights recorded during the experiments with Grane were somewhat lower than those observed for ANS, see Figure 63. The data is also here observed to be scattered. In addition, during the execution of the experiments with emulsified Grane, violent boilover that seemingly were more severe than for ANS 25% water-in-oil emulsion was observed. As a result, it can be seen in Figure 64 that the flame heights increased slowly after ignition of the oil slick, followed by a sharp increase of the flame heights, indicating the violent boilover.

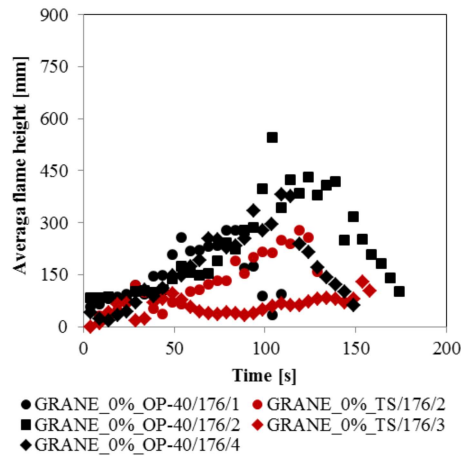


Figure 63: Average flame heights results as a function of time for Grane crude oil herded with OP40 and TS. Several experimental runs from Post-herding procedure.

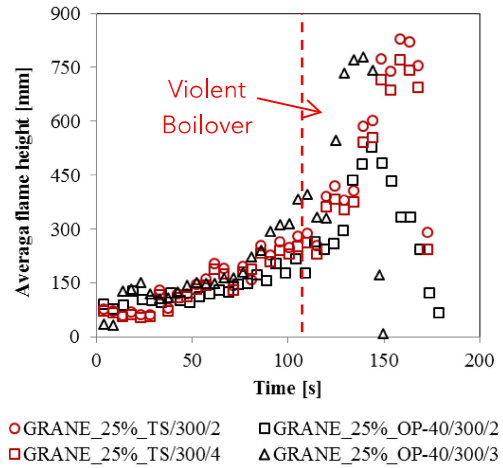


Figure 64: Average flame heights results as a function of time for emulsified ANS oil herded with OP40 and TS. Several experimental runs from Post-herding procedure.

5.2.2.6.2 Control experiments

The average flame height results obtained for the control experiments with ANS and its 25% water-in-oil emulsion are displayed in Figure 65, where a different behaviour than in previous experiments where the oil slick was allowed to drift during the burning can be seen. Three phases have been distinguished: a growing phase, followed by a seemingly steady phase, and, finally, a boilover phase where the flame heights increased significantly. The flame heights for Grane and its 25% water-in-oil emulsion, on the other hand, have a solely increasing tendency, as seen in Figure 66. During the experiments, boilover tendency was observed as in the previous cases with a violent boilover at the end of the experiments, followed by flame extinction.

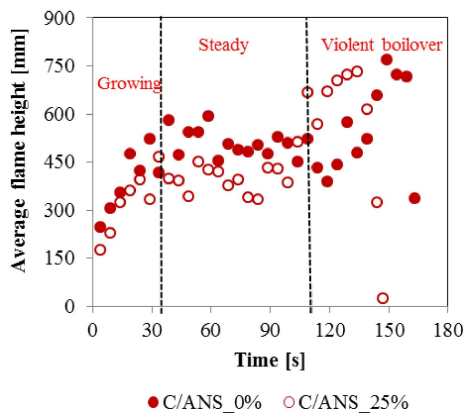


Figure 65: Average flame heights results as a function of time for ANS crude oil and its corresponding emulsion, under fully confined conditions (Control procedure).

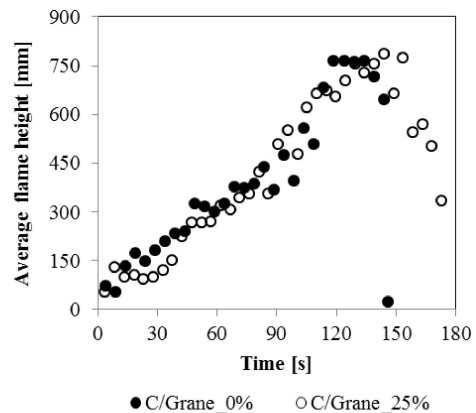


Figure 66: Average flame heights results as a function of time for Grane crude oil and its corresponding emulsion, under fully confined conditions (Control procedure).

5.2.3 Conclusions

Based on the obtained results from the experiments that were conducted, the following conclusions can be drawn:

- In general, ANS and Grane crude oils achieved relatively burning efficiencies of 37% and 21-26% respectively. These results are in line with other experimental results from similar studies with small amounts of oils. This is most likely due to experimental rig's differences during the burning of the oils where larger radiation and forced convection played a role. Furthermore, based on current data and large-scale data from other studies, there is a clear relationship between the size of the pool and the burning efficiency. For smaller oil amounts, lower burning efficiencies are achieved. On the other hand, for much larger oil amounts, larger burning efficiencies are obtained. It is expected that the results obtained by small-scale experiments can be extrapolated to large-scale scenarios.
- The burning efficiencies achieved by Grane are lower than those achieved by ANS, due to differences in the oil properties.
- The ANS and Grane 25% water-in-oil emulsions resulted in much higher burning efficiencies than those for fresh crude oils. More intense boilover was observed with sharp rise in flame heights during the burning of the emulsified oil slicks, it was estimated that between 12-18% and 18-28% is burned owing to intense boilover tendency for ANS and Grane respectively with regard to the fresh crude oils.
- For most of the small laboratory experiments the herding agent SilTech OP40 outperformed ThickSlick 6535.
- The herding Agent ThickSlick 6535 did not achieve as thick slicks as OP40, especially for Grane, and this is most likely due to sheen formation, which might have a buffering effect for the hydrocarbon based herder. In addition, two other possibilities may explain this poor performance, either the ANS crude differs significantly from previous samples, or the batch of ThickSlick 6535 was not properly formulated.
- The greatest slick thicknesses were achieved when the water was pre-treated with the herding agents. This is presumably due to an increased contact surface for the crude oil with the monolayer. Then TS was indeed able to thicken both crude oils with slick thickness above 3 mm, this results supports the sheen formation hypothesis. The possible buffer effect of sheen formations should be further studied since it may contribute to the TS's poor performance.
- In the long-term laboratory experiments, the monolayer produced by SilTech OP40 seemed to lose its surface tension properties after 60 minutes, after which point the effect of the herder declined and after 6-8 hours the oil slick thickness returned to initial conditions. ThickSlick 6535, on the other hand, could keep ANS and Grane oil slicks herded for up to 100 and 350 hours, respectively.

5.3 Physical Fate of Herder during Burning

The purpose of this part of the research project was to investigate the physical fate of the herder during burning. In the attempt to determine the physical fate, analyses of the herder were conducted after trial burns, i.e. fraction of herder remaining in the aquatic environment (water column and on the surface). Knowledge about the fate of the herder is important input to a full NEBA including the use of herders together with ISB. As can be seen from the results, this proved more difficult than anticipated when using standard tools and measures normally used in risk

assessments. One issue was related to the strong surface active preferences of the herders, which result in very different physical and chemical behaviour compared to other chemicals whose risk in the marine environment is normally evaluated.

5.3.1 Methods

The experiments were done as a two-step procedure: 1) samples were prepared and collected from laboratory burning experiments including herders for containment of the oil (for details see 5.2) in the laboratories of the Technical University of Denmark, during 2014-2015; 2) subsequent chemical analyses of these samples were undertaken to investigate and characterise the physical fate of the herder in the laboratories of DCE (Danish Centre of Environment and Energy) in 2015. The different variables in the experiments included are:

- Herder type (OP-40 and TS6535),
- Oil type (ANS and Grane),
- Emulsion (0 and 25 %)

From Material Safety Data Sheets (Appendix 1 and 2) it is stated that the specific gravity is 0.99 at 25°C and 0.9745 at 15°C for OP-40 and TS6535 respectively. The USEPA test results state that both are partially miscible in water.

OP-40 is a silicone based herder consisting of > 80% 3-(Polyoxyethylene)propylheptamethyltrisiloxane according to the MSDS. This copolymer is a commonly used silicone polymer and has a high thermal stability. It is also liquid at room temperature and characterised as a non-ionic amphiphilic copolymer (Kunieda et al. 2001). However, the remaining <20% of the OP-40 herder is unknown.

TS6535 is a hydrocarbon based herder consisting of 65 % Sorbitan Monolaurate and 35% 2-ethyl-1-butanol. 2-ethyl-1-butanol is an organic chemical compound slightly soluble in water and liquid at room temperature. Sorbitan Monolaurate is a detergent and monoester of lauric acid and hexitol anhydrides derived from sorbitol and also partly soluble in water.

More details about the herders can be found in Table 2 and Appendix 1 and 2.

The laboratory set-up and sample collection was based on expectations regarding the nature of the herders as outlined in Figure 67. The herders will quickly form a monolayer on the water surface due to their chemical structure, but could possibly in time degrade (biological, physical/chemical), evaporate, dissolve, disperse, entrain/dissolve in the oil (low oil solubility for the chemical oil herders is required as the herder otherwise would dissolve into the oil as shown by Garrett and Barger (1972)). Alternatively, the herders could also simply remain on the surface. Further, the burning of the oil slick could also have an impact on the fate of the herders and thereby change their original behaviour. The potential biodegradation in an Arctic environment is investigated and the results are described in Chapter 5.4.

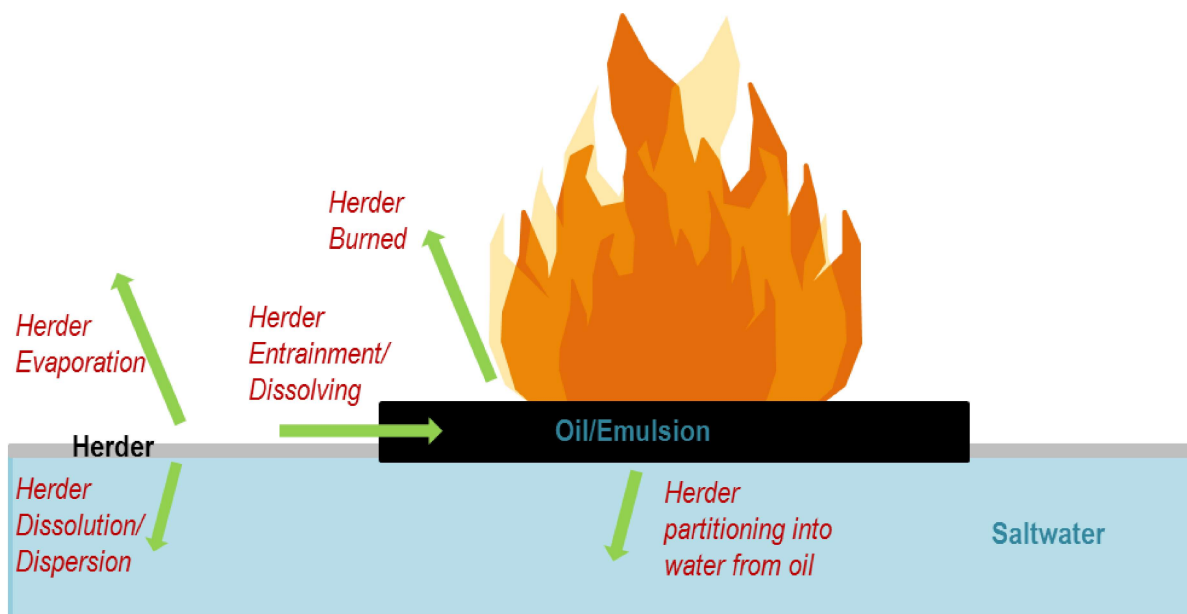


Figure 67: Conceptual outline of the potential herder fate processes during/after burning.

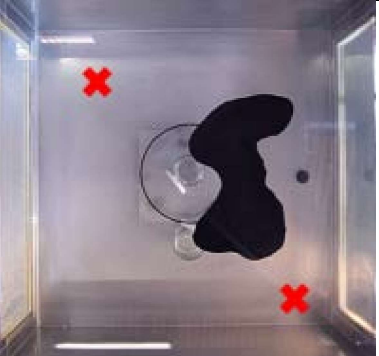

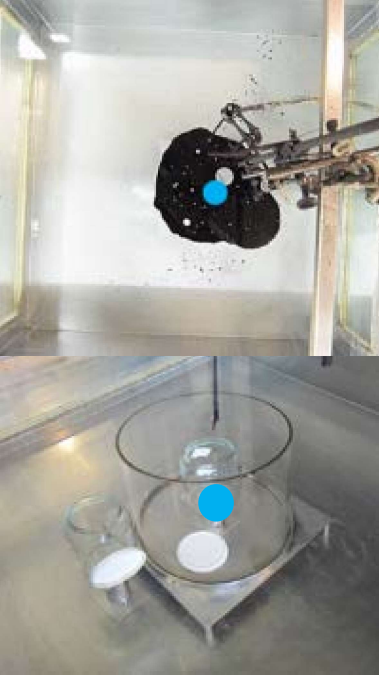
The burning experiments were performed on approximately 390 L of artificial saltwater (32 ‰, 0-2 °C) and approximately 170-250 g of oil herded with 150 µL of herder (corresponding to the prescribed real-world operational dosage of 150 µL/m² of water surface, which include a safety factor of three). The set-up is shown in Figure 68. Experiments were done with two crude oils (ANS and Grane), fresh oils and 25 % water-in-oil emulsions for both oil types and with two types of herders (OP-40 and TS6535). Triplicate experiments were done with each herder and oil type. Generally, the reproducibility of the experimental results is expected to be good within ±10% variation in the burning efficiency. Details about the procedures and results can be found in Chapter 5.2.1.

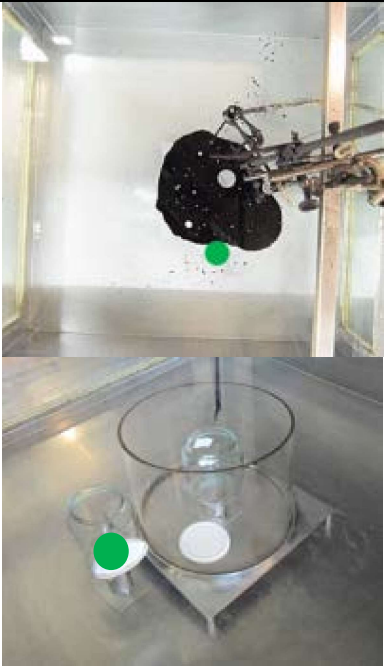
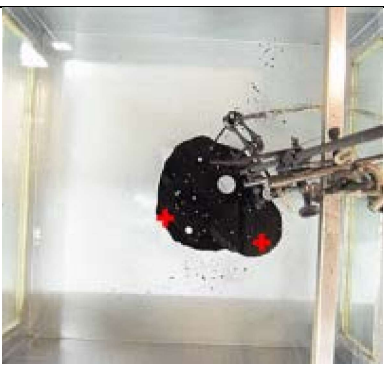


Figure 68: Illustration of the burning set-up during an initial trial burning.

Several samples were collected during each burning experiment for investigation of the fate of the herder and an overview is given in Table 8.

Table 8: Overview of samples collected during the execution of burning experiment to investigate the herder fate and illustration and explanation of the sampling.

Sample ID	Explanation of sample type and sampling method	illustration of sampling
Pre Burn Surface Water	<p>Surface water and herder, taken before ignition of oil slick.</p> <p>X marks the place of sampling of the water surface sample. The samples were taken in a red cap bottle that was dragged (approx. 30 cm) over the surface with the opening partial submerged.</p>	
Post Burn Surface Water	<p>Surface water taken after ignition and burning of oil slick. It might contain herder and oil residues due to boil-over.</p> <p>X marks the place of surface water sampling. The samples were taken in a red cap bottle that was dragged (approx. 30 cm) over the surface with the opening partial submerged.</p>	
Water Column - Below Oil Slick	<p>Water sample from below the oil slick after burning.</p> <p>O marks the place of water sampling beneath the slick.</p> <p>The jar was placed directly under the oil slick during burning of oil slick and the lid was closed under water.</p>	

<p>Water Column</p> <p>Water samples from the water column after burning.</p> <p>○ marks the place of water column sampling. The jar was placed under the oil slick but at the edge during burning of the oil. The lid was closed under water.</p>	<p>○ marks the place of water column sampling. The jar was placed under the oil slick but at the edge during burning of the oil. The lid was closed under water.</p>	
<p>Post Burn Oil</p> <p>Vials with oil/burn residue collected after burning.</p> <p>+ marks the place of oil sampling. The samples were collected with a small spatula in a small vial.</p>	<p>+ marks the place of oil sampling. The samples were collected with a small spatula in a small vial.</p>	

5.3.1.1 *Controlled small-scale evaporation experiments*

Small-scale evaporation laboratory experiments were conducted in the laboratories of DCE in 2015 in order to test the possible evaporation of OP-40. 10 steel dishes were filled with artificial made saltwater and OP-40 was applied to each dish corresponding to a concentration of 150 $\mu\text{L}/\text{m}^2$. During the 24 hours experiment the dishes were continually taken out and the content of water and herder were poured in closed bottles. The dishes were further rinsed with dichloromethane (DCM) in order to ensure quantitative transfer of the herder to the bottles. All samples were extracted and quantified as described in 5.3.1.2.

5.3.1.2 *Analytical chemical analyses at DCE*

It is the combined product (the complex herders) that are examined and not the single products in the herder. This approach is chosen as it is the whole herder product that is being released to the environment and also due to the fact that it parts of the herders are unknown.

Water samples were extracted three times with dichloromethane (DCM). For samples with a volume of 150-250 ml the extraction was with 1x 50 ml and 2x25 ml DCM. For larger samples with

a volume of 250-1000 ml the extraction was with 1x 100 ml and 2x50 ml DCM. The extracts were pooled, dried over Sodium Sulphate (Na_2SO_4), and concentrated by evaporation to 1 ml.

The water samples were analysed by GC-MS in SIM mode and quantified against external calibration standards. The GC-MS method was a further development of the GC method provided by Siltech (SAM-150 November 30, 2011). Column: HP5-MS, 30 m, diameter 0.25 mm, film thickness 0.25 μm , temperature program: 40°C 1 min, increase 8°C/min to 270°C, 270°C 20 min. Inlet temperature 280°C. Constant gas flow: 1 ml/min Helium. Injection standard: pyrene-d12. For quantification three significant peaks for each herder were selected. For OP-40: peaks at 18.32, 21.63 and 24.06 minutes. For TS6535: peaks at 23.02, 27.64 and 28.24 minutes. The mass ion (m/z) selected for SIM mode was 221 for OP-40 and 128 for TS6535 based on a full scan analysis of the herders, where the highest peaks in the chromatograms also were selected for quantification (see Figure 69). The chromatogram from the full scan analysis revealed that both herders consisted of a range of compounds which could be seen as peaks in the chromatograms (See Figure 70).

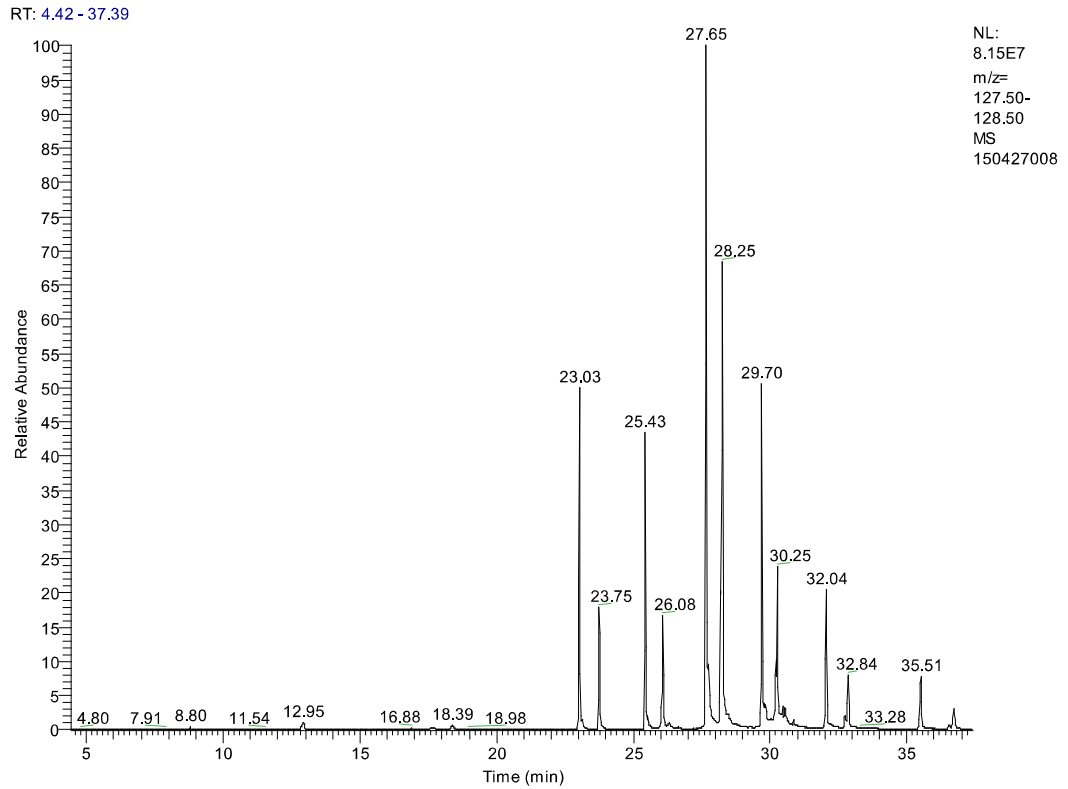
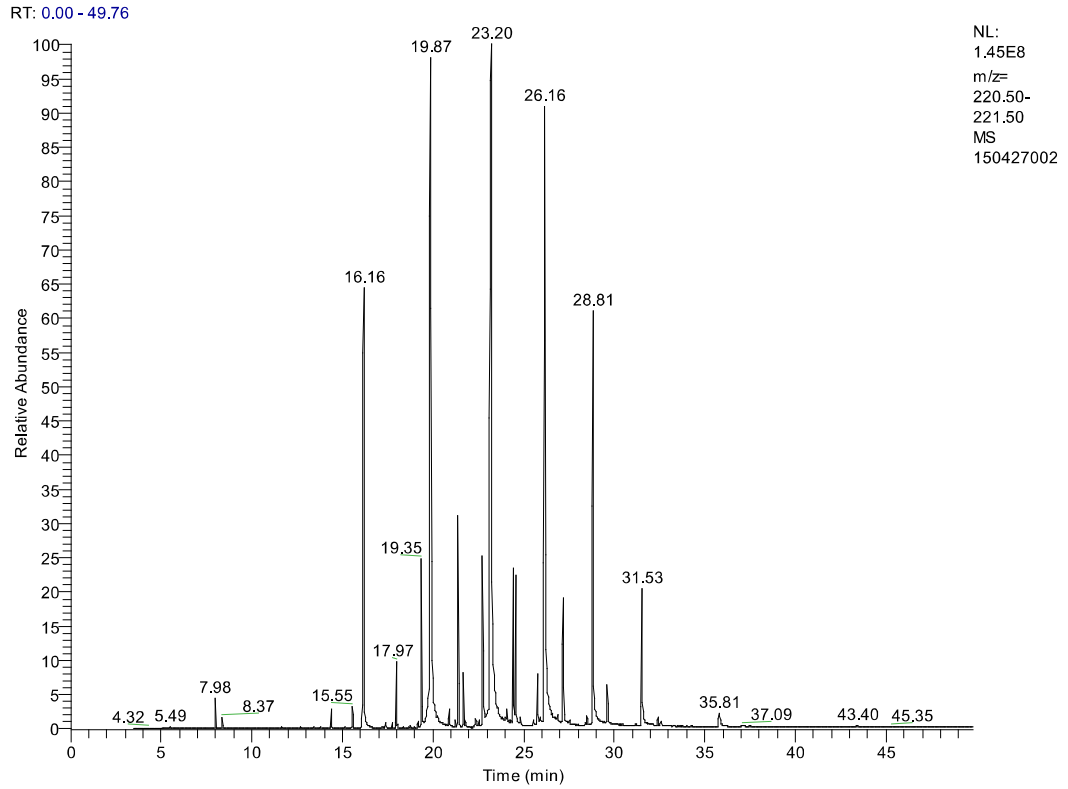


Figure 69: Chromatogram of OP-40 in SIM mode, mass ion (m/z) 221 at lower concentration level: 1 mg/ml (top) and Chromatogram of TS6535 in SIM mode, mass ion (m/z) 128 at lower concentration level: 1 mg/ml (bottom).

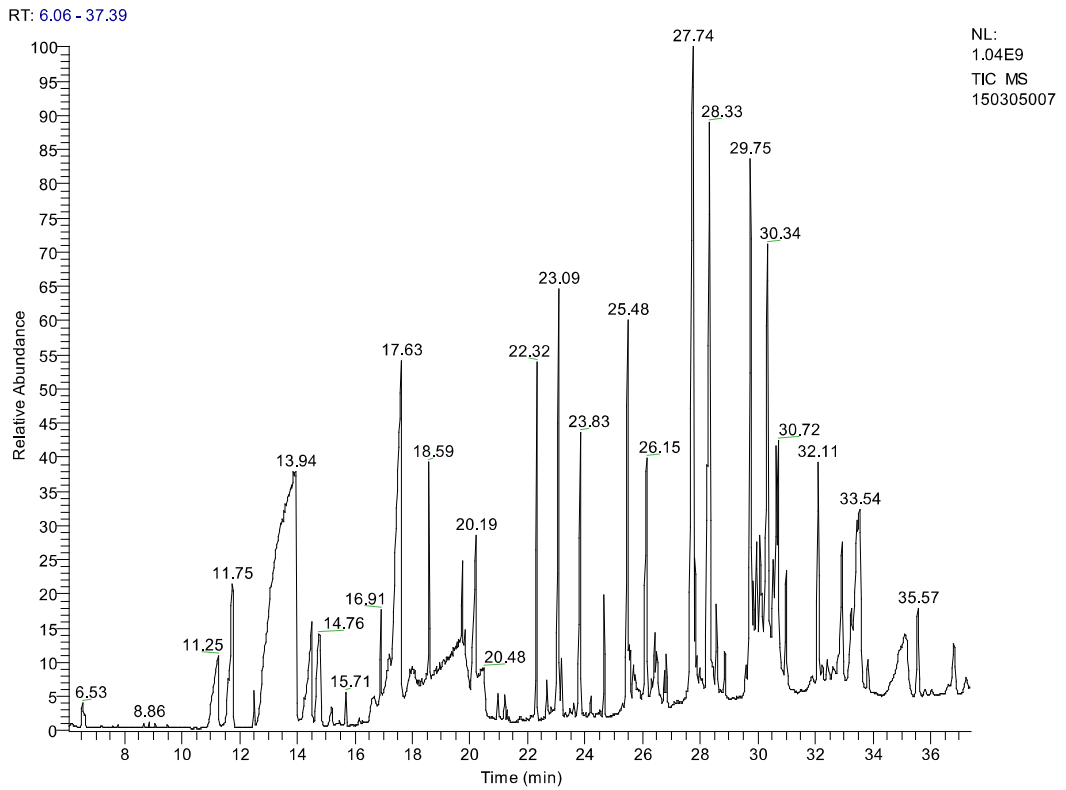
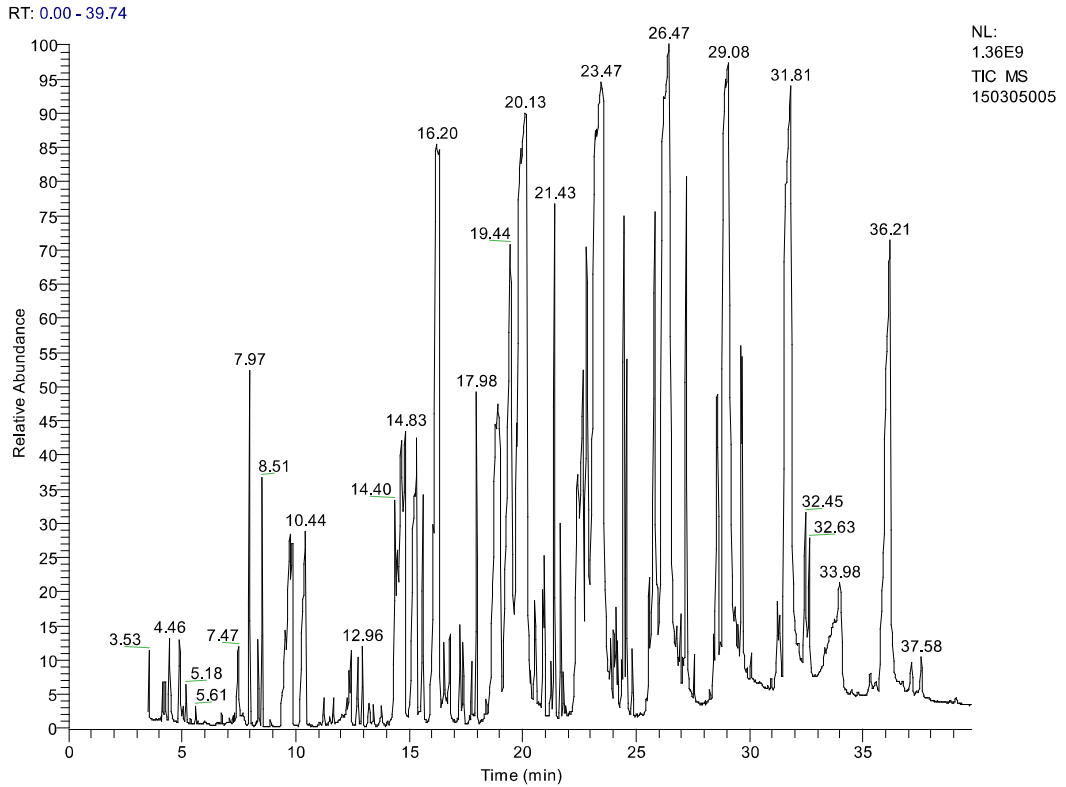


Figure 70: Chromatogram of OP-40 (top) and TS6535 (bottom) full scan analysis at high concentration level: 40 mg/ml.

Oil samples were diluted in DCM (200 μ l in 25 ml) and analysed by GC-MS in SIM mode and quantified against external calibration standards.

5.3.1.2.1 QA/QC

All glassware was heated at 450°C for 2 hours before use. Na_2SO_4 , glass wool and equipment that cannot tolerate high temperatures were cleaned by DCM before use. Blind samples and controls were analysed together with the experimental samples. The blind samples were true blinds which followed the exact same analytical procedure as the real samples. The controls were spiked water samples. There were typical one blind sample and one control per 4-10 samples. Average recovery from the controls; OP-40: 101%, TS6535: 99%, blind values average; OP-40: 0.1 $\mu\text{g/L}$, TS6535: <0.05 $\mu\text{g/L}$. Detection limit is 0.05 $\mu\text{g/L}$.

5.3.2 Results from the burning experiments

To determine the fate of the herders during burning a range of different samples from the burning experiments were analysed including:

- surface water before (but after herding) and after burning,
- water column samples after burning,
- water column samples from below the oil slick after burning
- oil samples from the oil slick before (but after herding) and after burning.

The content of herders in the water column samples are given as $\mu\text{g/L}$, surface water samples are given as $\mu\text{g/m}^2$ and oil samples are given as $\mu\text{g/g}$ oil.

The calculation of the herder concentrations on the surface is based on the estimations that each surface sample corresponds to approximately 0.015 m^2 . It is assessed to be unlikely that the sample size is larger than $2 \times 0.015 \text{ m}^2$ or less than $0.5 \times 0.015 \text{ m}^2$.

An overview of all the results is given in Figure 71 (water column), Figure 72 (surface) and Figure 73 (oil).

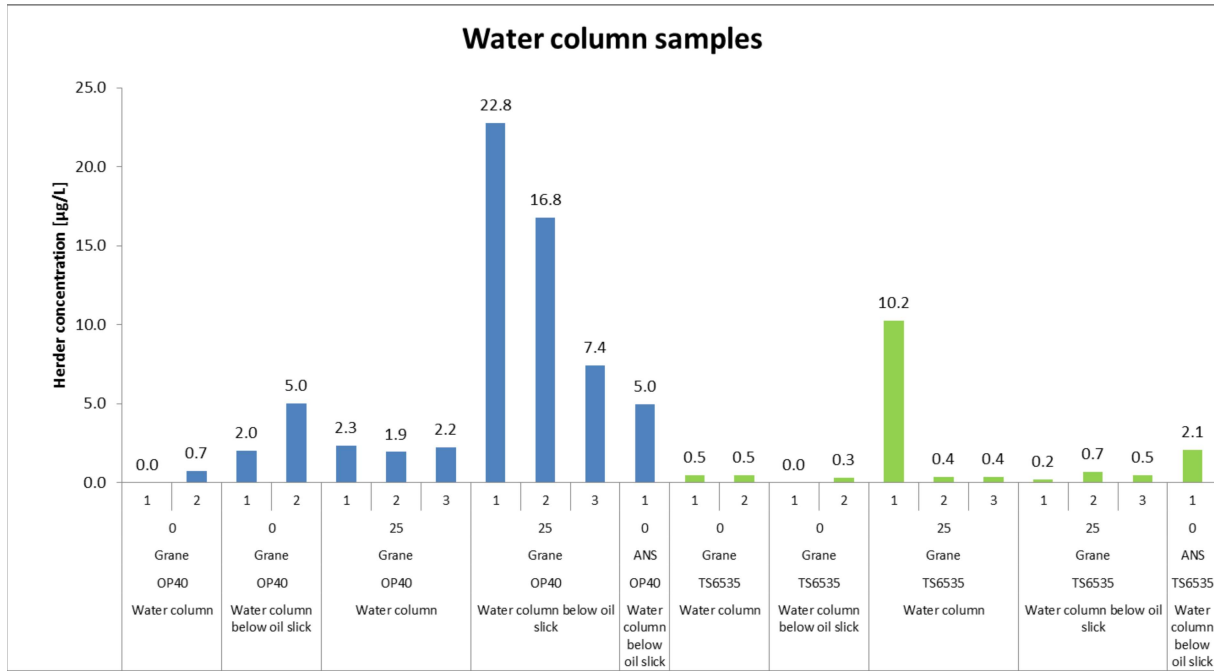


Figure 71: Concentrations of herders in different types of water column samples. 0 and 25 indicate 0 and 25 % w/O-emulsions. Blue columns are OP-40 and green columns are TS6535. Number 1-3 are experimental numbers. Sample ID explanations can be found in Table 8. Note that Grane 25 %, TS6535 (1), could be considered as an outlier.

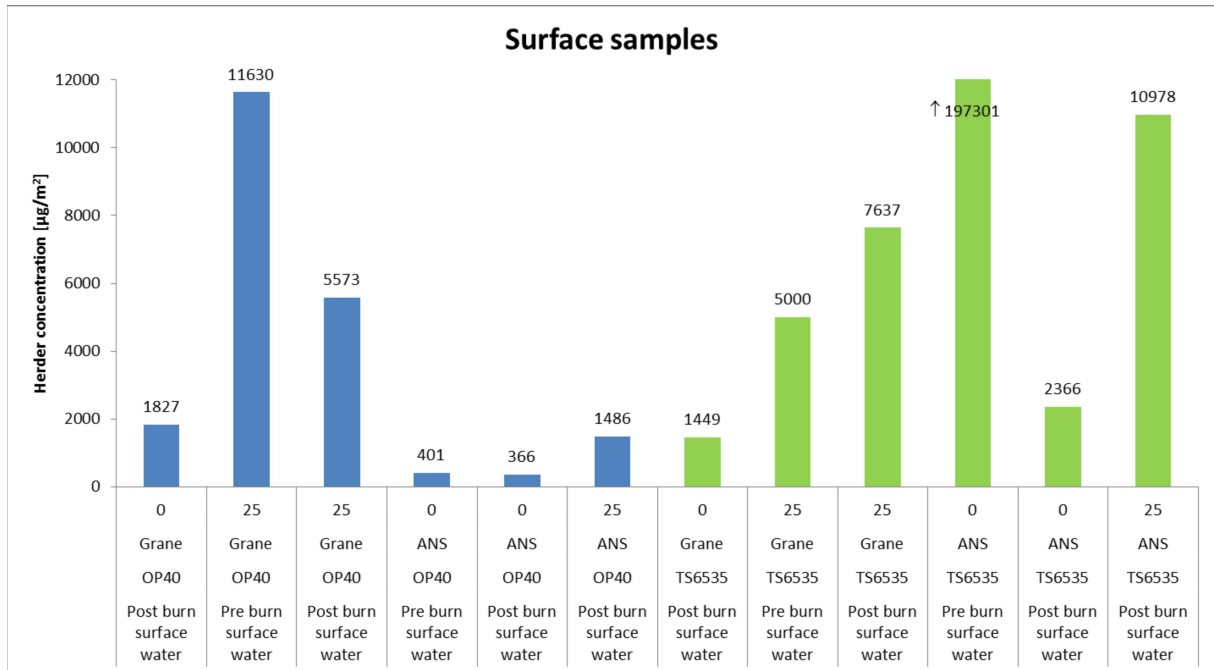


Figure 72: Concentrations of herders in different types of surface water samples. 0 and 25 indicate 0 and 25 % w/O-emulsions. Blue columns are OP-40 and green columns are TS6535. Sample ID explanations can be found in Table 8. Note that the value of ANS 0%, TS6535 is much higher than illustrated on the graph. The dose rate of herder for the experiments were 150 mg/m² which is the same as 150,000 µg/m².

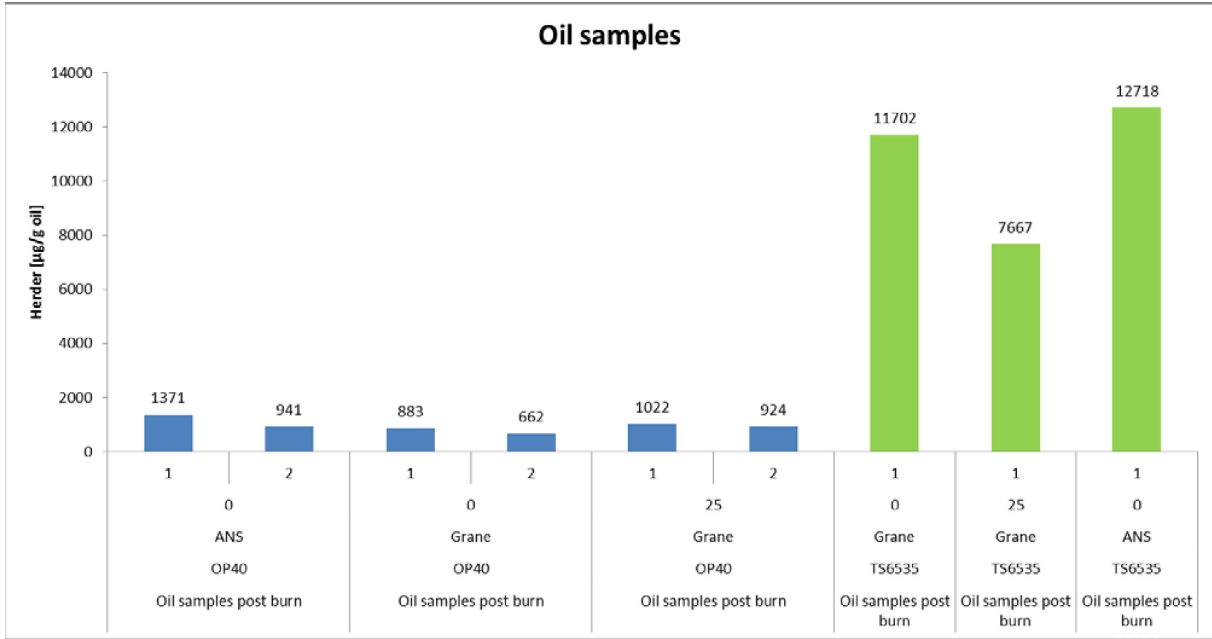


Figure 73: Concentrations of herders in oil residue samples taken after burning. 0 and 25 indicate 0 and 25 % w/O-emulsions. Blue columns are OP-40 and green columns are TS6535. Sample ID explanations can be found in Table 8.

Small concentrations of herders were found in the water column samples taken at the end of the experiment, approximately 60 minutes after herder application and subsequently burning. For Grane OP-40 25% emulsions relatively high concentrations have been measured. The results also indicate that samples taken directly under the oil slick are overall higher in concentration than the water column samples taken in the water column outside the oil slick. It is expected that the high concentration measured in the sample Grane 25% TS6535 (1) [10.2 µg/L] is due to sampling errors and should be considered as an outlier.

Generally the surface sample results indicate that after burning the herder is still found on the water surface. Large amounts of herder per surface area are measured in the water surface samples (pre and post burning) but generally large variations are shown in the results. The amount of herder applied in the experiments (150 µl) generates an excess of herder on the water surface, which could be seen as small droplets. Therefore, the herder was not uniformly distributed on the surface in the test tank. This was a challenge when taking samples from the surface. If droplets are sampled the measured concentrations will be much higher than the continuous herder layer on the surface. This is considered to be the explanation of the large variations in the measured amounts of herder in the surface water samples both pre and post burning. In spite of these variations there seems to be a tendency that the post burn water surface samples are slightly reduced in concentration compared to the samples taken before burning. However, due to the different sample types and heterogenic distribution of the herder on the water surface and water column, it was therefore not possible to make a mass balance of the herder after burning.

The results from the oil samples taken after burning (Figure 73) show that the highest concentrations of herder in the oil are found for TS6535. The two oil types tested in the experiments are quite different, with ANS constituting a medium gravity oil and Grane a heavy, asphaltenic crude oil. It should be kept in mind though that it was difficult to identify the herder peaks in the chromatograms due to the high concentration of different oil compounds in the burn residue and thus the results could therefore be overestimated.

5.3.3 *Discussion of fate of the herders during/after burning*

Based on the result from the burning experiments the fate of the herder during/after burning are discussed in the following with starting point in Figure 67.

5.3.3.1 *Dissolution/dissolving or partitioning into water*

All the water column sample results have been used to prepare Figure 74, where the maximum and minimum concentrations for the different types of samples (under or outside the herded oil slick) are gathered. Also the average concentration is given.

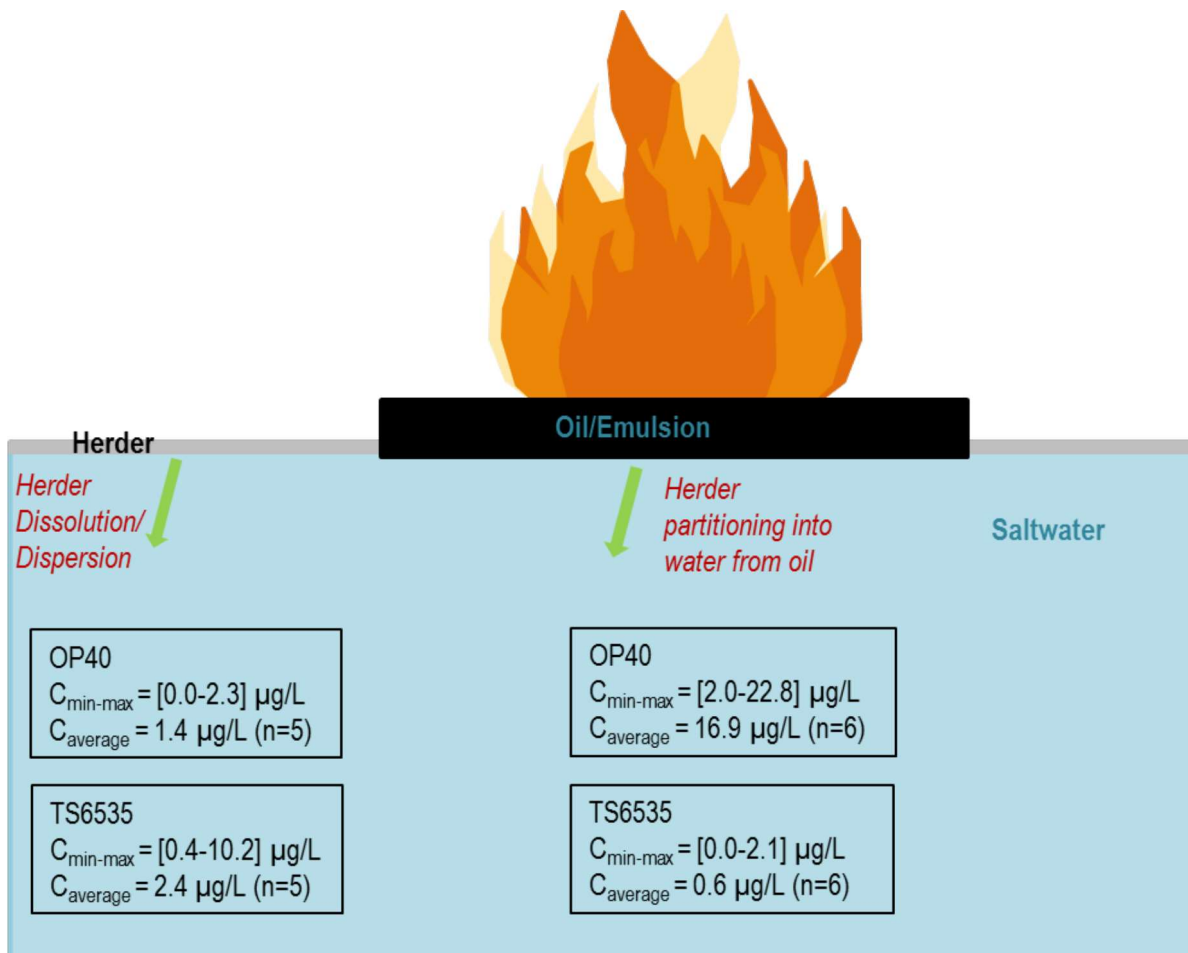


Figure 74: Minimum, maximum and average concentrations of the two herders found in the water column samples. Note that the high concentration measured in the sample Grane 25% TS6535 (10.2 $\mu\text{g/L}$) is expected to be due to sampling errors and should be considered as an outlier. If this sample is not included the numbers for TS6535 are $C_{\min-\max} = [0.4-0.5] \mu\text{g/L}$ and $C_{\text{average}} = 0.4 \mu\text{g/L} (n=4)$.

When the water column results for the two herders are compared, they indicate that OP-40 appears to be more soluble than TS6535, as higher concentrations of OP-40 were found in the water column and in the samples taken below the oil slick. This is not in accordance with the MSDS (Appendix 1 and 2) stating that OP-40 is insoluble whereas TS6535 is partly miscible, but is in accordance with the USEPA test results. Even though there might be high uncertainty related to which of the herders are expected to be most soluble, the findings of the herder in the water column are considered as valid, thus OP-40 as well as TS6535 was found to be mixed (dissolved/dispersed) into the water column during burning. The burning might be the process that could explain the concentrations found in the water column, even though the products are considered as insoluble/partly miscible. This becomes clearer when examining the samples from below the oil slick. For OP-40 it is clear that an increased concentration of herder is found beneath the oil slick after burning compared to the samples taken in the water column but outside the slick. For TS6536 the picture is not that clear and the concentrations under and outside the oil slick are comparable.

The increase in the concentrations of OP-40 found under the oil slick could also indicate that during burning oil droplets are released to the water and that herder attached to or dissolved into the oil would follow the submerged oil/water interface. The GC analyses support this as traces of oil components were found in the water samples.

If all the applied herder dissolved or dispersed homogeneously into the water column, the theoretical maximum concentration would be: $C_{\text{max conc theory}} = 385 \mu\text{g/L}$, since $150 \mu\text{L/m}^2$ was applied to a basin with 390 L water and a surface area of 1 m^2 . The sample with the maximum measured concentration was an OP-40 sample taken under the oil slick for the Grane 25% emulsion experiment and the measured concentration was $22.8 \mu\text{g/L}$. Based on these estimates, potentially 6% of the amount of the applied herder could partition out under the burning oil slick.

As written above the burning process is suggested to influence the solubility of the herder, thus it is suggested that experiments focusing solely on the herder fate without burning is conducted, to see if the same solubility data will be obtained. This is also relevant as the herder in the field is expected to cover a much larger area than would be affected by the combustion of the oil. The experiments in this report focus on the conditions close to the burn.

5.3.3.2 *Herding burn - fate during and after burning*

Based on visual observations from the video recordings both herding agents were able to re-thicken the oil slicks after flame out. No significant difference in the re-thickening efficiency was observed for both herding agents once the flames had died out. During the burning, the oil slick expands slightly and moves, most likely due to changes in the radiant heat that changes the surface and interfacial tension between the oil and the water. This could also be a result of physical removal of the herder by combustion. An attempt was made to directly ignite the herder both on ground and on a water surface without success. The herders appeared to evaporate and to some extent change colour, from colourless to white. However, more studies should be conducted to determine the fire properties of the herders.

The water surface samples indicate a tendency of reduction of the content of herder post burning. However, large variations were found within the results and are considered to be a consequence of the excess of herder seen as droplets on the water surface. It has been determined that $20 \mu\text{l/m}^2$ is the minimum effective herder dosage needed to contract the oil and this dosage is estimated to result in an average herder thickness of $0.02 \mu\text{m}$ or 200 \AA (Buist pers comm.) that equals $20,000 \mu\text{g/m}^2$. The monolayer thickness for OP-40 and TS6535 are estimated as 10 \AA and 30 \AA , respectively, based on the chemical structure and bond lengths (Buist pers comm.). This equals $1 \mu\text{l/m}^2$ for OP-40 and $3 \mu\text{l/m}^2$ for TS6535 which is approximately $1000 \mu\text{g/m}^2$ and $3000 \mu\text{g/m}^2$, respectively. No clear correlation is found between the measured amounts of herder per surface area (both pre and post burning) and the minimum effective dosage as well as the monolayer thickness dosage. Samples with both higher and lower content than the minimum effective thickness were measured in successful herding experiments. The explanation could be found in the nature of the herder layer: according to Garrett and Barger (1972) the excess drops of liquid film-forming chemicals do not spread on their own monolayers, but rather act as reservoirs to replace losses from the control film and to expand its size. Hence, the amount of herder on the water surface could differ, but $20 \mu\text{l/m}^2$ is the concentration required to maintain the herding effect. Consequently, excess herder is needed to contract the oil, and therefore it is expected that also droplets would form in the field as well, in spite of the unlimited potential spreading area. However, it is expected to be relatively short-lived. This is supported by field experiment results that have shown the herder can indeed contract the oil slick (SL Ross and DCE,

2014). Based on numbers from the field experiments, one trial included 631 L of crude oil herded with 3 L of herder. If all that herder would spread out forming a monolayer of 10\AA , a conservative estimation of the area affected would cover is approximately $3,000,000\text{ m}^2$.

Thus, it is concluded that not all of the herder is consumed during burning, even though the water surface samples indicates a tendency of reduction of the amount of herder (Figure 72), and that enough herder remains at the surface to re-thicken the oil once the fire extinguishes and “normal” surface and interfacial tensions between the oil and water have been re-established.

5.3.3.3 Evaporation with time

From the long-term herding experiments (Chapter 5.2.2.2.3) it is known that after a certain period of time the herder loses its ability to contain the oil. The long-term herding results for both crude oils and 25% water-in-oil emulsions shows that OP-40 was able to contain the oil for a relatively short period of approximately 2 hours: afterwards the oil slick thickness gradually declined and returned almost to the original thickness, after 10-12 hours. TS6535 on the other hand was able to contain the oil for a very long period of up to 100 hours and 350 hours for ANS and Grane, respectively. See Chapter 5.2.2.2.3 for further result details.

Since the long-term experiments were done on artificial saltwater it is assumed that the biodegradation are negligible. To verify if the decline in the herder ability is due to evaporation, the controlled small-scale evaporation experiment results were examined (Figure 75). The experiments were only made for OP-40 as this herder was able to contain the oil for the shortest period. The results suggest that some evaporation occurs with time and after 24 hours the evaporative loss was 44%, but not enough to reduce the concentration to below the minimum effective dose rate of $20\text{ }\mu\text{l}/\text{m}^2$. Also, much of the differences found in the measured values are also due to experimental variations and the relative uncertainty based on replicated measurements was estimated at 23%.

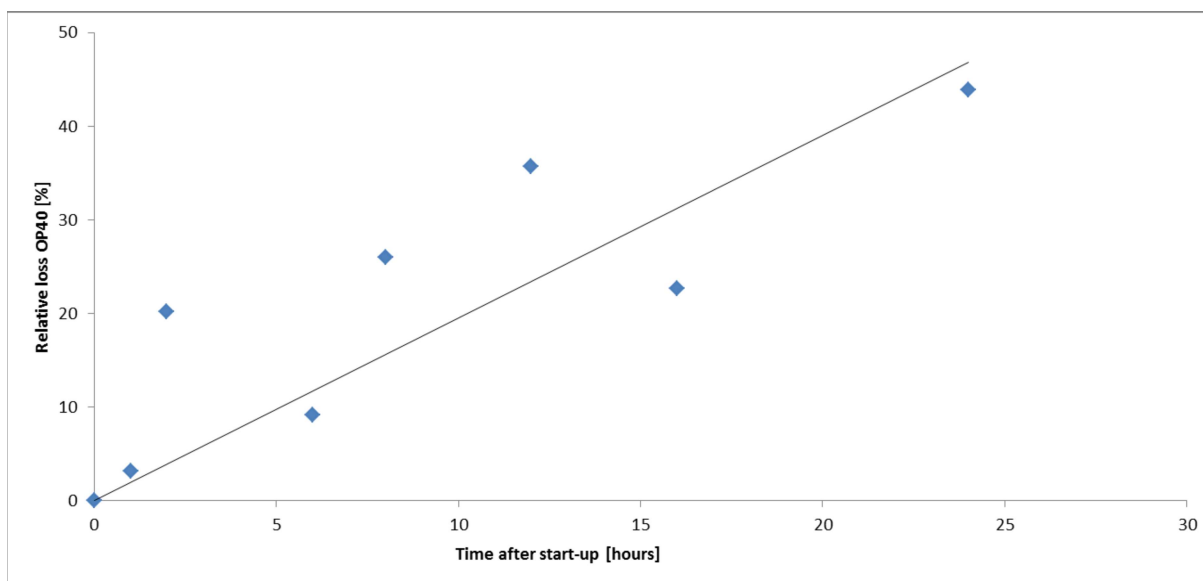


Figure 75: Relatively evaporative loss of herder (OP-40) in each container as a function of time.

The experiments were conducted at room temperature, thus it is assumed that the evaporation is expected to be even smaller in Arctic conditions with lower temperatures.

The main explanation for the loss of herding ability with time may thus be ascribed to a combination of the different processes also including dissolution/dispersion into the water and/or physical/chemical degradation of the herder. In the presence of oil it is also likely that the herder is dissolved/entrained into the edge of the oil slick, which could also reduce the efficiency of the herder with time (see below for further discussions).

5.3.3.4 *Herder entrainment/dissolving*

As already described the decaying effectiveness of the herders with time could be a result of the herder dissolving into the edges of the oil slick. Both herders were also detected in the oil samples.

The burning experiments with emulsified oil (25 % water-in-oil emulsions) indicate that the emulsion might impact on the herder concentrations found in the different compartments. In the post burn samples the concentrations on the surface water and in the water column below the oil slick are higher for emulsions than for crude oils. This is seen for both oil types.

An explanation could be related to the nature of the herder and the emulsions. The herder is expected to follow the oil/water interface due to its chemical structure with a hydrophilic end and a hydrophobic end and thus it is suggested that the herder will follow the oil/water interface into the emulsions. To burn emulsions, the water must be removed by either evaporation or breaking of the emulsions first, the latter could potentially lead to release of herder with the water from the emulsions, thus resulting in increased herder concentrations. From Chapter 5.2.2.1 it is given that the burning efficiencies for ANS and Grane 25% water-in-oil emulsions are higher than those for pure ANS and Grane. The temperature of the emulsified oil layer increased due to the heat transfer from the oil burning layer, which is able to boil off all or a part of the encapsulated water droplets. As a result, this can trigger a violent boilover at the end of the burning process, producing a sharp increase in the flame height.

5.3.4 *Conclusions*

- Small concentrations of herders were found in the water column samples taken at the end of the experiment.
- For the post burn samples, water surface and water column, the concentrations are highest when the test oil is emulsified. This was noted for both oil types.
- Samples taken directly under the oil slick had overall higher concentrations, in particular for OP-40.
- Generally, after burning, the herder was mainly found on the water surface, though reduced in amount compared to pre burning.
- The herders were able to re-thicken the oil after flame out.
- Long-term herding experiments showed that OP-40 was able to contain the oil for a period of approximately 2 hours: afterwards the oil slick thickness gradually declined and returned almost to the original thickness, after 10-12 hours. TS6535 was able to contain the oil for a very long period of 100 hours and 350 hours for ANS and Grane respectively.
- The decaying effectiveness of the herders with time is ascribed to be a combination of the different processes: evaporation, dissolved/entrained into the edge of the oil slick and a minor dissolution/dispersion into the water.

5.4 Toxicity and Bioaccumulation of Herders in High Arctic Copepod and Biodegradation of Herders in Arctic Surface Waters

The environment and biology in Arctic waters are characterized by low temperatures in surface waters throughout the year, large seasonal variations in solar radiation, high prevalence of sea ice, a unique animal and plant life adapted to the cold climate and life associated with the sea ice, general slow biological processes, short food chains and a high content of lipids (fats) in the organisms. The relative high content of lipids / fats serves partly as an energy reserve to withstand long periods without food and partly as insulation against the cold environment. The existing knowledge about chemical herders' effects and bioaccumulation on Arctic organisms is very sparse. The only environmental impact studies conducted with the herders are preliminary standard biodegradation and toxicity laboratory tests (SLRoss and DCE 2015). Such toxicity and bioaccumulation of chemicals is typically based on tests with temperate and tropical species, as is biodegradability which is normally tested at temperatures between 15 and 25 °C.

The purpose of the present work was to study the toxicity and bioaccumulation of the herders ThickSlick 6535 (TS6535) and Siltech OP-40(OP-40) on high Arctic copepod (*Calanus hyperboreus*), as well as to study the biodegradation of the herders in Arctic waters at low temperature. No standard Arctic test organisms exist. However, *Calanus hyperboreus* has been chosen as it is the key species in the Arctic regions because of its abundance and essential role in the Arctic food web and is therefore representative as a test organism for studying effect of chemicals in the Arctic environment. The copepod has been used previously in similar studies with success (Hjorth and Nielsen 2011; Nørregaard et al. 2014; Nørregaard et al. 2015)

Also, no standards exist for toxicity on Arctic organisms. To cope with these challenges a science based approach was followed in the design of the experimental set-up for the toxicity tests. It should be kept in mind that the experiments have been conducted in a well-equipped but simple on-site field laboratory. It was decided to do the experiments in field to secure sufficient high fitness of the organisms, as the long transportation from Greenland to Denmark is expected to stress the organisms unnecessarily.

The biodegradation experiments are conducted according to the OECD 309 Guideline for testing of chemicals - Aerobic Mineralisation in Surface Water – Simulation Biodegradation Test (OECD 309) (Appendix 3). This guideline is designed in such a way that makes it possible to also investigate biodegradation at Arctic conditions and with Arctic organisms.

In the guideline (OECD 309 – Appendix 3) it is written in Paragraph 23 that: "If unavoidable, stock solutions of non-volatile substances with poor water-solubility should be prepared by use of a volatile organic solvent, but the amount of solvent added to the test system should not exceed 1% v/v and should not have adverse effects on the microbial activity. The solvent should not affect the stability of the test substance in water". Since the chemical herders have a strong preference for a surface or interface rather than going into solution, acetone was used to prepare stock solutions to ensure that the herders were homogeneously dissolved in the water. The concentrations of acetone used (0.02%) are well below the limits reported for effects seen from acetone in different test standards (ECCTOC 1996) and thus acetone is not expected to impact on the results. Without the use of stock solutions of herders in acetone, the herders will not go into the water phase and the test results will be misleading and would have indicated that the herders cannot be biodegraded and that the herder is not toxic because it never were in contact with the copepods. Thus, the following results represent data about the inherent properties of the herders in relation to biodegradability, bio-accumulation and toxicity in Arctic conditions.

Using Arctic organisms also meets the OECD guideline in terms of duration of test periods. Such data are essential in an environmental risk assessment of the chemicals in combination with how the environment is potentially exposed in a real scenario.

5.4.1 Methods

5.4.1.1 Toxicity and bioaccumulation of herders on high Arctic copepods

Toxicity and bioaccumulation of herders was studied on copepods (*Calanus hyperboreus*) collected in Disco Bay at Arctic Station Greenland in April 2015 (Figure 76). Sampling of copepods was conducted in Disco Bay approximately 1 nautical mile from Qeqertarsuaq through a hole cut in the sea-ice (Figure 77) at a 300-m-deep station (N69° 13.386 W53° 25.218) using a WP-3 net (200 µm mesh size) with a non-filtering cod-end.

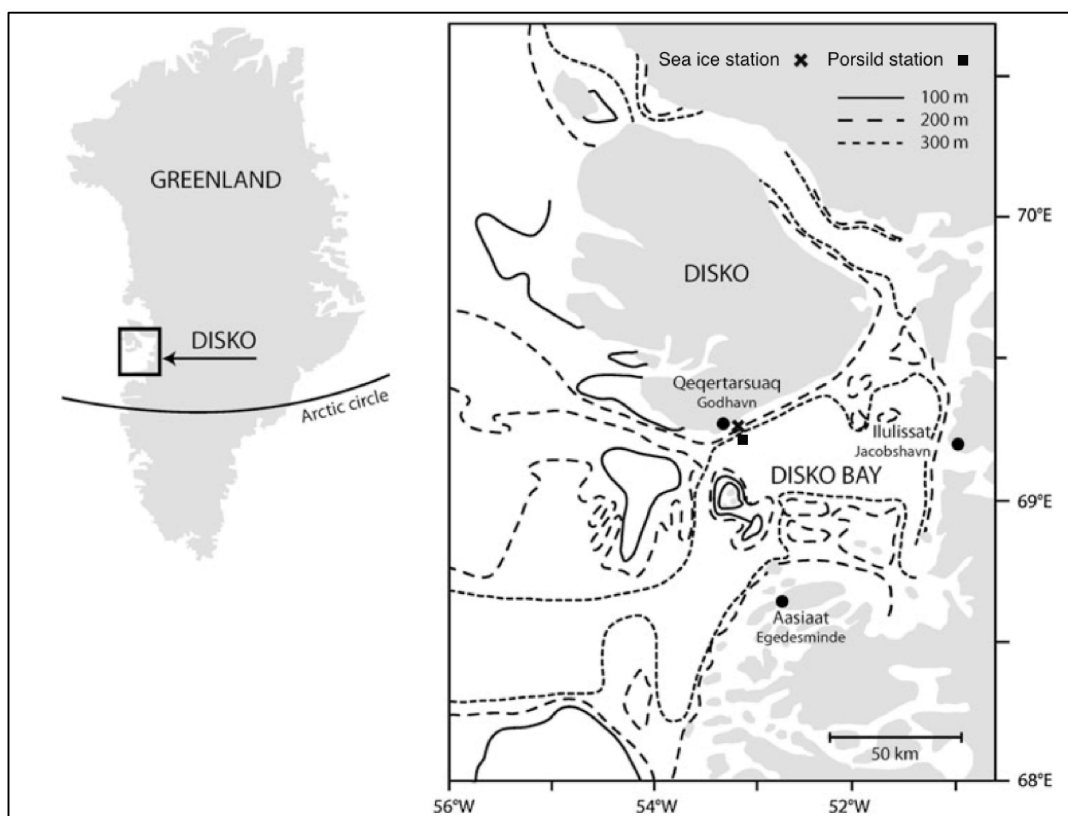


Figure 76: Sampling site for copepods and water approximately 1 nautical mile from Qeqertarsuaq (N69° 13.386 W53° 25.218).

Water was collected with a 30 L Niskin bottle at 50 meters depth and stored in thoroughly cleaned plastic buckets (Figure 77). Before use the seawater was filtered first through a 10 µm mesh size filter then through a 0.45 µm mesh size filter to remove organism and particulate matter.

After collection, the copepods were stored in the dark and at in situ temperatures for approximately 4 hours in a thermos-box before sorting. The experiments were performed on only adult copepods, sorted out manually in the field laboratories of the Arctic Station (Figure 78).



Figure 77: Sampling of copepods and water from a hole in the sea ice approximately 1 nm from land.



Figure 78: *Calanus hyperboreus* for chemical analysis

The incubation tests (both toxicity and bioaccumulation) were done in 1 litre redcap glass bottles at 2°C in the dark. Ten adult individuals were added to each bottle at the start of the experiment. At the start and after seven days food, consisting of natural phytoplankton from the fjord, was added to the water in the test bottles. The incubation test bottles were placed in a temperature-controlled container at the Arctic Station, Disko to ensure Arctic conditions with 2 °C.

Stock solutions of herders were made in acetone at 0.48, 2.4, 12, 60 and 300 mg herder/ml acetone. The stock solutions were stored at -20°C.

In the study adult *Calanus hyperboreus* were exposed to 0.096, 0.48, 2.4, 12 and 60 mg /L of TS 6535 (n=3) or OP-40 (n=3). Controls and acetone controls were included. Amount of acetone in the test bottles was 0.02%, which is well below the limits reported for effects seen from acetone in different test standards (ECETOC 1996; OECD 203). Supplementary toxicity testing was conducted with a concentration of 600 mg/L of TS6535. The range of test concentrations was selected based on results from the study performed by Environmental Enterprises (Environmental Enterprises, 2012). The short-term (acute) and long-term (chronic) effects of herders on behaviour and mortality were observed over a period of 25 days. Dead animals were harvested continuously for measuring the body herder residue. At the end of the experiment all the remaining and living *Calanus hyperboreus* were harvested also for determining the body residue herder concentrations. The herder concentration in the water was measured at day 1, 4 and 25.

5.4.1.2 *Biodegradability of herders at Arctic condition*

Surface water was collected with a 30 L Niskin sampler through a hole cut in the sea ice at 5 meters depth and stored in thoroughly cleaned plastic buckets. The sampling site was approximately 1 nautical mile from Qeqertarsuaq - (N69° 13.386 W53° 25.218) and the sampling took place in April 2015. Before use the Arctic surface water was screened through a 100 µm mesh size net for removing large particles. Subsequent the degradation of the two herders by the natural assembles of bacteria was followed over 28 days at 2°C. The incubation was done in 1 litre redcap glass bottles placed in the dark at 2°C. The studies were according to the OECD 309 Guideline for testing of chemicals - Aerobic Mineralisation in Surface Water – Simulation Biodegradation Test (OECD 309 – Appendix 3). According to the OECD Guideline 309 degradation was studied in concentration <100 µg/L to minimize the risk of inhibition of the bacterial activities by the herders. The studies include controls, acetone controls, sterile controls (formalin) and reference controls (degradation of C14 radiolabel benzoate), also in accordance with the OECD 309 guideline. The amount of acetone in the test bottles was 0.004% and thus well below the limits reported for effects seen from acetone in different test standards (OECD 309). The purpose of the acetone controls was to examine possible adverse effects caused by the acetone towards the microbial population indicated by the degradation of the reference substance.

5.4.1.3 *Analytical chemical analyses at Danish Centre for Environment and Energy (DCE) – Water samples*

Water samples were extracted three times with dichloromethane (DCM). For samples with a volume of 150-250 ml the extraction was with 1x 50 ml and 2x25 ml DCM. For samples smaller 1x25 and 2x10 ml DCM.

The water samples were analysed by GC-MS in SIM mode and quantified against external calibration standards. The GC-MS method was a further development of the GC method provided by Siltech (SAM-150 November 30, 2011). Column: HP5-MS, 30 m, diameter 0.25 mm, film thickness 0.25 µm, temperature program: 40°C 1 min, increase 8°C/min to 270°C, 270°C 20

min. Inlet temperature 280°C. Constant gas flow: 1 ml/min Helium. Injection standard: pyrene-d12. For quantification three significant peaks for each herder were selected. For OP-40: peaks at 18.32, 21.63 and 24.06 minutes. For TS6535: peaks at 23.02, 27.64 and 28.24 minutes. The mass ion (m/z) selected for SIM mode was 221 for OP-40 and 128 for TS6535 based on a full scan analysis of the herders, where the highest peaks in the chromatograms also were selected for quantification.

5.4.1.3.1 QA/QC

All glassware was heated to 450°C for 2 hours before use. Na₂SO₄, glass wool and equipment that cannot tolerate high temperatures were cleaned by DCM before use. Blind samples and controls were analysed together with the experimental samples. The blind samples were true blinds which followed the exact same analytical procedure as the real samples. The controls were spiked water samples, with concentration of OP40: 22.1 µg/L and TS: 27.1 µg/L. Only one concentration level was used to have a statistical basis. There were typical one blind sample and one control per 4-10 samples. Average recovery from the controls; OP-40: 101%, TS6535: 99%, blind values average; OP-40: 0.1 µg/L, TS6535: <0.05 µg/L. Detection limit is 0.05 µg/L

5.4.1.4 Analytical chemical analyses at Danish Centre for Environment and Energy (DCE) – copepod samples

The copepods were extracted by Soxhlet extraction with 500 ml dichloromethane (DCM) for 12 hours. Each sample consisted of a mixture of 12 copepods, which is equivalent to a sample amount of approximately 0.4 g. The extracts were concentrated by evaporation to 1 ml.

The samples were analysed by GC-MS in SIM mode and quantified against external calibration standards. The GC-MS method was a further development of the GC method provided by Siltech (SAM-150 November 30, 2011). Column: HP5-MS, 30 m, diameter 0.25 mm, film thickness 0.25 µm, temperature program: 40°C 1 min, increase 8°C/min to 270°C, 270°C 20 min. Inlet temperature 280°C. Constant gas flow: 1 ml/min Helium. Injection standard: pyrene-d12. For quantification three significant peaks for each herder were selected. For OP-40: peaks at 18.32, 21.63 and 24.06 minutes. For TS6535: peaks at 23.02, 27.64 and 28.24 minutes. The mass ion (m/z) selected for SIM mode was 221 for OP-40 and 128 for TS6535 based on a full scan analysis of the herders, where the highest peaks in the chromatograms also were selected for quantification.

5.4.1.4.1 QA/QC for Copepods

All glassware was heated at 450°C for 2 hours before use. Na₂SO₄, glass wool and equipment that cannot tolerate high temperatures were cleaned by DCM before use. Blind samples were analysed together with the experimental samples. No controls were included due to lack of a proper matrix. The blind samples were true blinds which followed the exact same analytical procedure as the real samples. There was typical one blind sample per 5 samples. Blind values average; OP-40: 0.4 µg/g, TS6535: 0.5 µg/g. Detection limit is 0.1 µg/g.

5.4.2 Results

The concentration in the stock solutions was verified by chemical analyses and the results can be found in Tables 9 and 10. The chemical analysis confirms that the measured concentrations in the stock solutions are close to the nominal concentrations of both TS6535 (Table 9) and OP-40 (Table 10). In addition the results indicate that the addition of the herders to the test bottles is accurate.

Table 9: Nominal and measured concentration of TS 6535 in the stock solutions.

TS6535	Nominal	Measured	Unit
STAM 1 TS	300	299	mg/ml
STAM 2 TS	60	73	mg/ml
STAM 3 TS	12	11	mg/ml
STAM 4 TS	2,4	2,5	mg/ml
STAM 5 TS	0,48	0,45	mg/ml

Table 10: Nominal and measured concentration of OP-40 in stock solutions.

OP-40	Nominal	Measured	Unit
STAM 1 OP-40	300	279	mg/ml
STAM 2 OP-40	60	57	mg/ml
STAM 3 OP-40	12	12	mg/ml
STAM 4 OP-40	2,4	2,3	mg/ml
STAM 5 OP-40	0,48	0,48	mg/ml

5.4.2.1 Results - Toxicity and Bioaccumulation of herders on high Arctic copepods

Effects of the herders on behaviour and mortality of *Calanus hyperboreus* was observed over a period of 25 days. A distinct mortality was seen at the highest test concentrations of the herders. After 1 day 100% mortality (LC-24h) was seen at 600 mg/L for TS6535, and at 12.5 and 60 mg/L for OP-40. Markedly sub-lethal effects (EC-48h, very slow moving animals) were seen after 48 hours exposure in concentrations of 12.5 mg/L and 60 mg/L TS6535, as well at 2.4 mg/L OP-40. More than 90% mortality was subsequent seen after 25 days at 2.4 mg/L OP-40 and 60 mg/L TS6535 (LC-25d) (Table 11). Mortality in controls and acetone controls were on average < 5% indicating that acetone addition did not influence the results.

Table 11: LC and EC for TS6535 and OP-40 on *Calanus hyperboreus* after 24 and 48 hours, and 25 days (end of the experiment and based on the nominal concentrations)

	24h- LC	48h – EC	25d – LC
TS6535	<600 mg/L	<12.5 mg/L	<60 mg/L
OP-40	< 12,5 mg/L	<2.4 mg/L	<2.4 mg/L

The effect concentrations found for *Calanus hyperboreus* are on the same order of magnitude as reported by Environmental Enterprises (Environmental Enterprises, 2012) for *Mysidopsis bahia* and *Menidia beryllina* (Table 12) determined in static standard toxicity test at temperature at 24°C. The estimated LC values in the study by Environmental Enterprises are also based on the nominal concentrations as we did.

Table 12: Effect concentrations* of TS6535 and OP-40 on *Mysidopsis bahia* (mysid) and *Menidia beryllina* (fish) determined in static standard test at temperature at 24°C.

	<i>Mysidopsis bahia</i>			<i>Menidia beryllina</i>		
	48-hr LC50	95% Interval	Confidence	96-hr LC50	95% Interval	Confidence
ThickSlick 6535	286 mg/L	226-363 mg/L		138 mg/L	121-157mg/L	
OP-40	6.83 mg/L	5.75-8.77 mg/L		3.33 mg/L	2.88-3.84 mg/L	

* the estimated effect concentrations are based on nominal concentrations. Note that the concentrations are not measured in stock solution, test bottles or organisms.

Exposure and accumulation of lipophilic substances can be critical, especially for high Arctic organisms like *Calanus hyperboreus* with a high fat content, and where internal exposure may be large in starving periods. The MSDS sheet includes very little information: OP-40 is listed as insoluble in water and TS6535 as partly miscible in water. No data (e.g. K_{ow}) is found for evaluation of the bioaccumulation potential for TS6535 and OP-40. Based on SMILES notations of the chemicals in the herders both herders are estimated to have lipophilic properties (EPIWIN, US EPA) for accumulation/storing in lipids of the organisms.

Nominal and measured concentrations of herders in test water and recovery rates and estimated bio- concentrations are shown in Table 13. It should be noted that recovery rates are low and in particularly for TS6535. The low recovery can be attributed to the poor solubility of the herders in water and that the herder might partition to the surface film or the tendency of the herders to adsorb on surfaces of the test bottles. Alternatively, and most likely, fast degradation/decomposition could be the explanation. For details about the biodegradation see Chapter 5.4.2.2. Bio-Concentrations Factor (BCF) estimates, based on nominal concentrations and measured concentrations of herders in the water, are shown in Table 14. The estimates for BCF indicate that OP-40 might bioaccumulate and TS6535 might not bioaccumulate in the high Arctic copepods.

5.4.2.2 Results - Biodegradability of herders in Arctic waters

Biodegradation of the herders was measured by chemical analysis of water samples taken day 7, 14, 23 and 28 and the measured concentrations are shown in Table 15 and Table 16.

It should be pointed out that TS6535 could only be detected in the "Sterile control" sample where formalin was added for elimination of the microbial degradation activity. The preliminary data indicates that either the microbial degradation was very fast and all TS6535 was degraded within the first 7 days, or that TS6535 quickly and strongly adsorbs to the surface of the test bottles. The constant concentration of TS6535 in "Sterile control" indicates that the physical / chemical degradation of TS6535 is insignificant. Also analyses on extracts from test bottles at the end of the experiment (Day 28) indicate that the adsorption to glass surface of the test bottles is insignificant. And therefore fast degradation is most likely the explanation on the findings in Table 14.

The concentrations in OP-40-100 µg/L test bottles and "Sterile control" were constant over time. This indicates that degradation of OP-40 in concentration of 100 µg/L was insignificant. The decline in concentrations of OP-40 of 20 µg/L might indicate some degradation between Day 23 and Day 28.

Table 13: nominal and measured concentrations of herbicides in test water, as well as recovery rates in percentage.

	Day	Nominal concentration (mg/L)	Measured concentration in water (mg/L)	Recovery rates (%)
OP-40	1	60	45.090	75.2
OP-40	1	12.5	5.078	40.6
OP-40	4	2.4	0.422	17.6
OP-40	4	0.48	0.114	23.8
OP-40	25	0.48	0.129	26.9
OP-40	4	0.096	0.012	12.5
OP-40	25	0.096	0.024	25.0
TS6535	1	600	305.017	50.8
TS6535	4	60	3.723	6.2
TS6535	25	60	0.158	0.3
TS6535	4	12.5	0.019	0.2
TS6535	25	12.5	0.000	0.0
TS6535	4	2.4	0.001	0.0
TS6535	25	2.4	0.000	0.0
TS6535	4	0.48	0.004	0.8
TS6535	25	0.48	0.000	0.0
TS6535	4	0.096	0.004	4.3
TS6535	25	0.096	0.000	0.0

Table 14: bioconcentration factor (BCF) calculated as ratios between body residue in *Calanus hyperboreus* and nominal concentration and measured concentration of herders in waters respectively.

	Day	Nominal concentration (mg/L)	Measured concentration in water (mg/L)	Body residue (mg/kg ww)	BCF - Nominal conc. (L/kg)	BCF - Measured conc. (L/kg)
OP-40	1	12.5	5	600	48	118
OP-40	1	60	45	4444	74	99
OP-40	25	0.096	0.024	1.0	10	42
OP-40	25	0.48	0.129	2.5	5	19
TS6535	1	600	305.017	1036	2	<1
TS6535	25	0.096	0	3.2	34	-
TS6535	25	0.48	0	2.4	5	-
TS6535	25	2.4	0	3.5	1	-
TS6535	25	12.5	0	2.5	0	-
TS6535	25	60	0.158	106	2	670

Table 15: Concentration of TS6535 in test bottles at day 7, 14, 23 and 28 (µg/L).

Test concentration - TS6535	Replicate	Day 7	Day 14	Day 23	Day 28
20 µg/L	1	0.00	0.00	0.00	0.00
20 µg/L	2	0.00	0.00	0.00	0.00
20 µg/L	3	0.00	0.00	0.00	0.00
20 µg/L	Mean	0.00	0.00	0.00	0.00
100 µg/L	1	0.00	0.01	0.00	0.00
100 µg/L	2	0.00	0.00	0.00	0.00
100 µg/L	3	0.00	0.00	0.00	0.00
100 µg/L	Mean	0.00	0.00	0.00	0.00
Formalin - 100 µg/L	1	24.39	27.54	24.62	15.83
Formalin - 100 µg/L	2	14.65	27.79	20.54	26.44
Formalin - 100 µg/L	3	28.13	35.42	22.37	16.82
Formalin - 100 µg/L	Mean	22.39	30.25	22.51	19.69

Tabel 16: Concentration of OP-40 in test bottles at day 7, 14, 23 and 28 ($\mu\text{g/L}$).

Test concentration - OP-40	Replicat e	Day 7	Day 14	Day 23	Day 28
20 $\mu\text{g/L}$	1	5.89	7.70	6.86	5.90
20 $\mu\text{g/L}$	2	8.52	7.90	9.75	4.33
20 $\mu\text{g/L}$	3	7.75	7.15	7.91	3.14
20 $\mu\text{g/L}$	Mean	7.38	7.58	8.18	4.46
100 $\mu\text{g/L}$	1	47.49	47.64	49.73	50.98
100 $\mu\text{g/L}$	2	56.04	54.89	62.76	59.20
100 $\mu\text{g/L}$	3	46.03	50.61	55.12	56.86
100 $\mu\text{g/L}$	Mean	49.85	51.05	55.87	55.68
Formalin - 100 $\mu\text{g/L}$	1	61.38	56.64	66.10	63.93
Formalin - 100 $\mu\text{g/L}$	2	65.19	60.83	58.80	63.85
Formalin - 100 $\mu\text{g/L}$	3	64.11	60.27	55.26	64.20
Formalin - 100 $\mu\text{g/L}$	Mean	63.56	59.25	60.05	64.00

EMURC (2013) did some initial biodegradation work with TS6535 and OP-40. TS6535 is rapidly biodegraded (>60% gone in 6 days) and OP-40 is not (<25% gone in 25 days). The result of present study confirms this characterization of the biodegradability of the herders.

Degradation of reference substance benzoate (C14 radiolabels) with and without addition of acetone was tested according to OECD 309 Guideline for validation of the test. The results in Figure 79 show that after a short lag phase about 80% of the benzoate was degraded over the 28 days. The distinct degradation of reference substance passes the validation criteria in OECD 309 Guideline and shows that the addition of acetone did not inhibit the degradation.

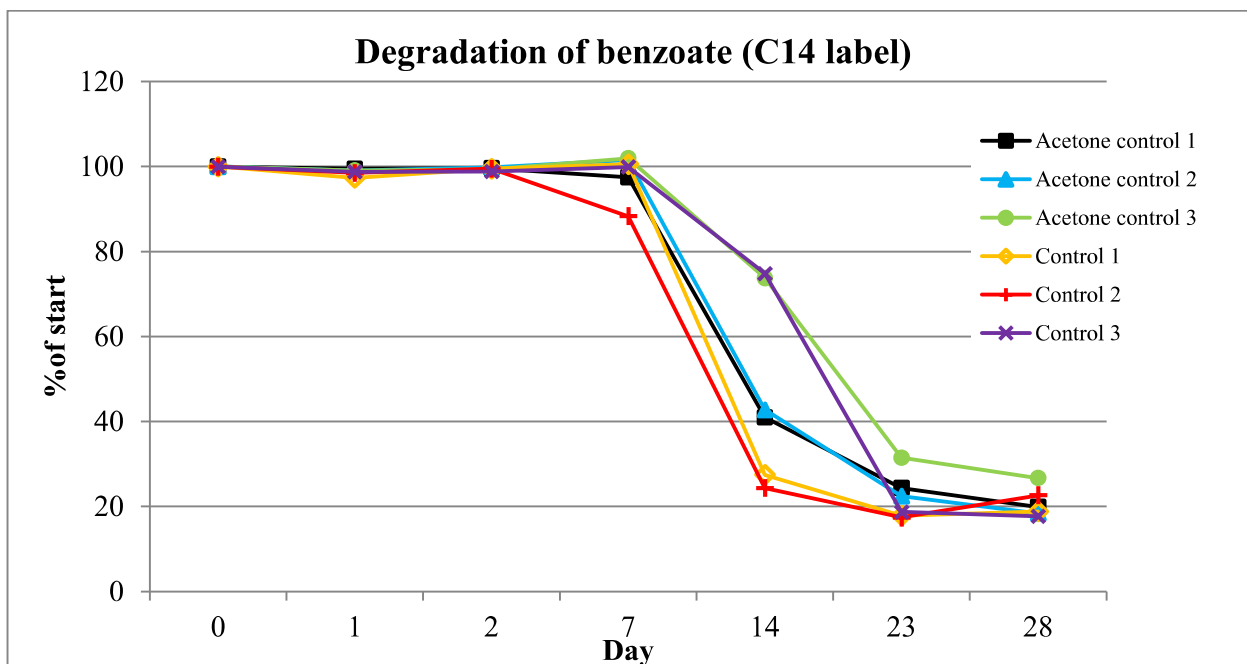


Figure 79: Degradation of the reference substance benzoate (C14 radiolabelled) with and without addition of acetone.

5.4.3 Conclusions

The environment and biology in Arctic waters are characterized by low temperatures in surface waters throughout the year, large seasonal variations in solar radiation, high prevalence of sea ice, a unique animal and plant life adapted to the cold climate and life associated to the sea ice, generally slow biological processes, short food chains and a high content of lipids (fats) in the organisms. The existing knowledge about chemicals' degradation and effects in the Arctic environment is very sparse.

The purpose of the present work was to study toxicity and bioaccumulation of the herbicides TS6535 and OP-40 on high Arctic copepod (*Calanus hyperboreus*), as well to study the biodegradation of the herbicides in Arctic waters at low temperature.

The experiments were conducted according to the OECD 309 Guideline for testing of chemicals - Aerobic Mineralisation in Surface Water – Simulation Biodegradation Test (OECD 309 – Appendix 3). The following findings were made based on the investigations of the inherent properties of the herbicides in relation to biodegradability, bio-accumulation and toxicity in Arctic conditions and with Arctic organism meeting the OECD guideline in relation to also duration of test periods. Such data are essential to be evaluated in an environmental risk assessment of the chemicals in combinations with how the environment is potentially exposed in a real scenario.

The result of the study indicated that the degradation of OP-40 was insignificant or low over 28 days in Arctic waters. TS6535 disappeared quickly in the test bottles probably due to rapid biodegradation.

Effects of herbicides on behaviour and mortality of *Calanus hyperboreus* were observed over a period of 25 days. A distinct mortality was seen at the highest test concentrations of the herbicides. After 1 day 100% mortality was seen at 600 mg/L TS6535. Markedly sub-lethal effect (very slow moving animals) was seen after 48 hours exposure in concentrations of 12.5 mg/L and 60 mg/L

TS6535. More than 90% mortality was subsequent seen after 25 days at 60 mg/L TS6535. Corresponding 100% mortality was seen at 12.5 and 60 mg/L OP-40 and sub-lethal effect after 48 hours exposure in concentrations of 2.5 mg/L OP-40. More than 90% mortality was subsequent seen after 25 days at 2.5 mg/L OP-40. To put these results in context, it should be noted that all of these effect concentrations of herders in water are several orders of magnitude greater than the herder concentrations measured underneath the test slicks in the Crude Oil Flammability Apparatus (e.g., see Figure 71 in Section 5.3.2).

The nominal effect concentration for *Calanus hyperboreus* are in the same order of magnitude as the nominal effect concentrations reported by Environmental Enterprises (Environmental Enterprises 2012) for *Mysidopsis bahia* and *Menidia beryllina* determined in static standard toxicity test. The result indicates that OP-40 may bioaccumulate and TS6535 may not bioaccumulate in the high Arctic copepods.

It should be noted that TS6535 was difficult to measure and that some uncertainty must be attributed to the results due to the poor solubility of the herders in water and that herders have a great tendency to be caught in the surface film, as well as degrade fast (TS6535). Also, it must be noted that the studies on herders are complicated by the poor solubility and derived poor distribution of herders in water.

5.5 Impacts of Herders on Feathers from Arctic Sea Birds

5.5.1 Methods

The laboratory experiments included exposure tests of seabird feathers in sheens of herders followed by measurements of the feather microstructure disruption following a modified methodology of O'Hara and Morandin (2010), and changes in weight as a result of absorption of water, herders and/or oil. The exposure experiments were conducted in the laboratories of DCE – Danish Centre of Environment and Energy from December 2014 to summer 2015.

The Arctic sea bird carcasses, Thick-Billed Murre (*Uria lomvia*) and Common Eider (*Somateria mollissima*), were bought in Nuuk, Greenland from legally hunted seabirds. The skin including the feathers from the chest of the birds were carefully removed and the samples were transported to Denmark in sealed boxes. The feathers were removed from the skin in the laboratory with forceps and stored carefully to avoid any unwanted disturbances of the feather structure.

The samples for testing were:

- Fresh samples of: herders (TS6535 and OP-40), oil (Alaska North Slope - ANS) and a mixture of herder and oil
- Post burn samples i.e. surface fraction of oil (ANS) residue/herder mixture from burning experiments herded with OP-40 and TS6535 respectively. For details regarding the preparation of the burn residues see description in 5.2.
- Controls: seawater, solvent (Dichloromethane = DCM)

Different dosages of herders were used:

- A. 1 $\mu\text{L}/\text{m}^2$ which is the dose estimated to results in a monolayer for OP-40 (corresponds to 10 Å)
- 3 $\mu\text{L}/\text{m}^2$ which is the dose estimated to results in a monolayer for TS6535 (corresponds to 30 Å)

- B. 20 $\mu\text{L}/\text{m}^2$ which is the minimum effective dose that can contract oil, based on laboratory tests (Buist, 2015 pers. communication).
- C. 150 $\mu\text{L}/\text{m}^2$ which is the application dose specified to contract the oil in field/large scale oil spill operations. This recommended application dose rate includes a safety factor of three.

An overview of the samples for the exposure tests is given in Table 17 and Table 18. All the samples were made in triplicates or more. Different dilutions of the oil/residue samples were used and the corresponding film thicknesses have been estimated based on the assumption that the oil/residue was homogeneously distributed over the test water surface area. The thicknesses for the herders have not been estimated. From knowledge about the fate of the herder it is assumed that the herder ultimately will spread out forming a monolayer of 10 Å or 30 Å for OP-40 and TS6535 respectively. However, excess droplets of herder will be seen for the B and C herder dosages. Garrett and Barger (1972) write that droplets will not spread over their own monolayer, but the droplets will act as reservoirs to replace losses from the control film and to expand its size. Therefore it is expected that the thickness of the herder will range from a monolayer (10 Å to 30 Å) to the application dose thickness (0.15 μm or 1500 Å) or even higher where the excess herder droplets is found, until the herder has completely spread out to a monolayer. Thus, it is expected that the monolayer thickness will be the dominant thickness of the herder area. From a field experiment including 631 L of crude oil herded with 3 L of herder (SL Ross and DCE, 2014), it is estimated that if the herder spread to a 10 Å monolayer it would cover approximately 3,000,000 m^2 (3 km^2). In the laboratory however, the area was limited by the size of the different test containers and thus represent situations where the herder has not spread out completely and excess herder is still found on the water surface – which could be considered as worst-case / conservative situations.

Table 17: matrix for the herder only exposure experiments. The same types of experiments were done for both Common Eider and Thick-Billed Murre and in triplicate.

Sample description	Sample size	Water surface area
A - OP-40 Monolayer dosage	1.7 μL	1.7 m^2
A - TS6535 Monolayer dosage	5.1 μL	1.7 m^2
B - OP-40 Minimum effective thickness dosage	2.2 μL	0.11 m^2
B - TS6535 Minimum effective thickness dosage	2.2 μL	0.11 m^2
C - OP-40 Application dosage	1.5 μL	95 cm^2
C - TS6535 Application dosage	1.0 μL	95 cm^2

Table 18: Sample matrix for the exposure experiments on feathers of seabirds (Common Eider and Thick-Billed Murre).

Sample description	Water surface area [cm ²]	Herder [μL]*	Estimated sample thicknesses** (oil /residue) [μm]					
			0	1	2	3	4	5
Dilutions***			0	1	2	3	4	5
Seawater	95		-	-	-	-	-	-
DCM	95		-	-	-	-	-	-
Crude ANS	95		1.16E+01	1.16E+00	1.16E-01	1.16E-02	1.16E-03	-
Residue ANS (herded with OP-40)	95		8.60E+00	8.60E-01	8.60E-02	8.60E-03	8.60E-04	-
Residue ANS (herded with TS6535)	95		1.07E+01	1.07E+00	1.07E-01	1.07E-02	1.07E-03	-
ANS + OP-40	95	1.5	-	1.16E+00	1.16E-01	1.16E-02	1.16E-03	1.16E-04
ANS + TS6535	95	1.0	-	1.16E+00	1.16E-01	1.16E-02	1.16E-03	1.16E-04

*corresponding to the application dosage of approximately 150 μL/m² (C).

** The oil/residue film thicknesses have been estimated based on the assumption that the oil/residue was homogeneously distributed over the test water surface area.

*** The dilution factor is based on log-10 transformed dilution, e.g. 1 corresponds to 10 times dilution

5.5.1.1 Exposure experiments on seabird feathers procedure

The following procedure was used during all the exposure experiments. Each sample was done in triplicates.

1. A container is filled with seawater (30 ‰).
2. The test sample (see details below) is applied to the surface of the seawater with a micropipette.
3. The feather is weighed and the weight is noted. Subsequently the feather is placed on the surface film in the Petri dish for 15 sec. with a pair of tweezers. Thereafter the feather is drawn three times over the surface (to simulate mechanical stress) and finally the feather is placed on the surface for 15 sec.
4. The feather is re-weighed and the weight is noted.
5. The feather is placed on a glass plate, with the convex surface upwards. A smaller glass plate is placed over the tip of calamus (shaft of the feather) to fix the feather.
6. The feather is photographed four places, with two places on each side of the middle and one overall reference photo. See Figure 80.

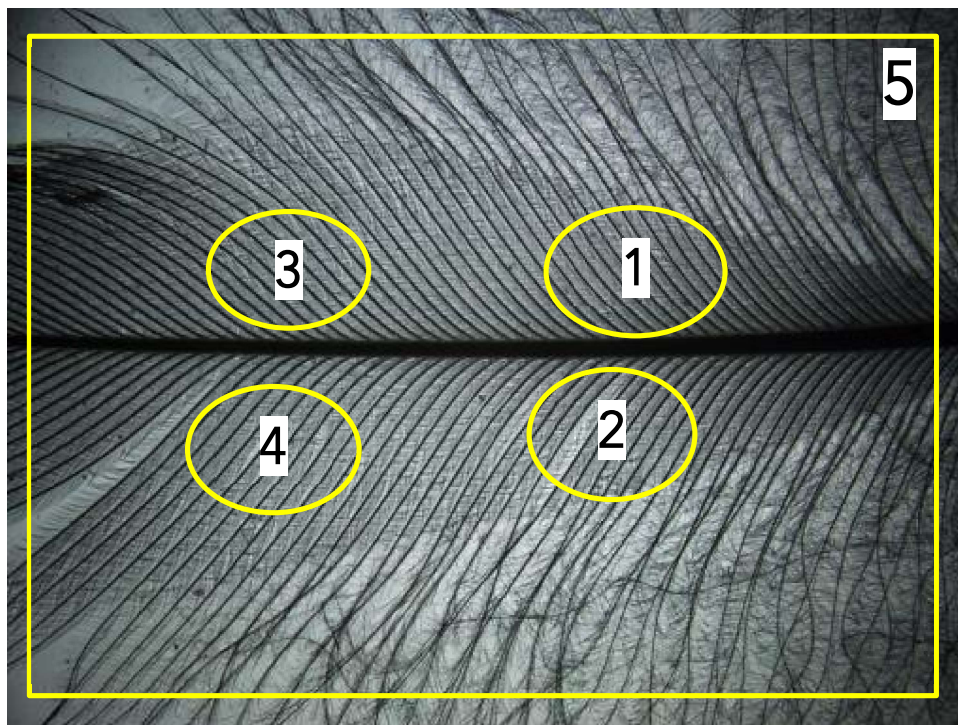


Figure 80: Indication of where the five pictures (The numbers 1-5) are taken. For the detailed pictures (1-4) a magnification of 1x11.25 was used. The width of One of the detailed pictures is 1.7 mm.

Different containers were used for the experiments. For the application herder dosage experiments (C) and all the experiments including oil/residue a Petri dish (11 cm D) was used. However, to be able to apply the small amounts for the two other dosage experiments (A and B) the scale of the experiments was increased and therefore the monolayer dosages (A) were applied to a children's swimming pool filled with seawater and the minimum effective dosage (B) were applied to a seawater surface in a cake dish. Illustrations of the experimental set-up can be seen in Figure 81.

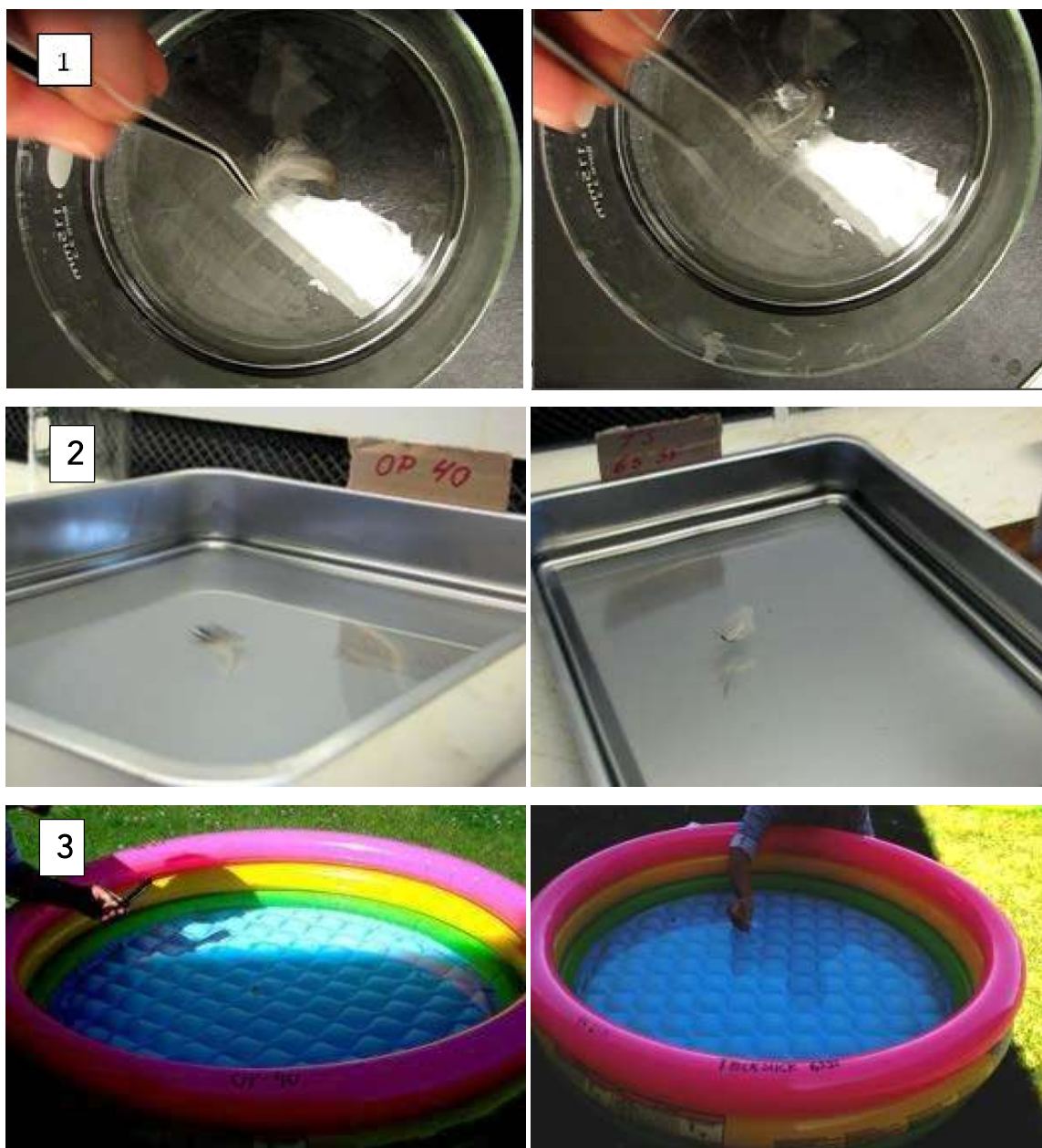


Figure 81: Examples of the application dosage experiments - C (1), minimum effective thickness dose experiments - B (2) (Note that the feather in the OP-40 experiment is sunken) and monolayer thickness dose experiments – A (3).

The monolayer dose (A) experiments took place outside. The weather was nice with little wind, sun and 25 °C. The minimum effective thickness (B) and application dosage (C) experiments were made in the laboratory. The salinity of the seawater was 31 ‰.

5.5.1.2 Sample preparation

5.5.1.2.1 Herders

ThickSlick 6535 and OP-40 were applied directly to the seawater surface and the exposure procedures were as described above.

The herders were stored in the refrigerator and then warmed to room temperature prior to experiments to ease the handling of the otherwise relatively viscous herders.

5.5.1.2.2 Crude oil

Alaska North Slope (ANS) is a medium grade crude oil, with a specific density of 0.8939. Details about the physical/chemical composition of ANS can be found in Table 1. During the experimental period (approximately 2 months), the oil was stored in the refrigerator.

The dilution series were made as follows: 4.92 g of ANS was put into a red-cap bottle and filled with 25 mL of DCM. The dilution series were made from this stock solution to 10, 100, 1000 and 10,000 times dilutions. The corresponding thicknesses can be found in Table 18.

0.5 mL of the sample was carefully transferred to the Petri dish with a glass micropipette on the inner side of the dish, to make sure that the sample positioned on the seawater surface and keep DCM from sinking. The set-up was left for at least 5 minutes to allow for the DCM to evaporate completely. The exposure procedure was as prescribed above.

5.5.1.2.3 ANS burn residue

The burn residue samples from the burning experiments (see Chapter 5.2.1) were absorbed to a 3M sorbent pad in a glass jar. 25 mL DCM were transferred to the glass jar with a pipette and stirred carefully for 30 minutes. The 3M sorbent pad was removed and dried for 24 hours before weighing. Less than 5 % of the burn residue was left on the 3M absorption pad with this extraction method.

The dilution series were made from the burn residue in the glass jars (stock solutions): 3.76 g ANS residue-OP-40 /25 mL DCM and 4.69 g ANS residue-ThickSlick6535/25 mL DCM to 10, 100, 1000 and 10,000 dilutions. The corresponding thicknesses can be found in Table 18.

0.5 mL of the sample was carefully transferred to the Petri dish with a glass micropipette on the inner side of the dish, to make sure that the sample positioned on the seawater surface and keep DCM from sinking. The set-up was left for at least 5 minutes to allow for the DCM to evaporate completely. The exposure procedure was as prescribed above.

5.5.1.2.4 Oil + Herder

The dilution series were made as follows: 4.92 g of ANS was applied to a red-cap bottle and filled with 25 mL DCM. The dilution series were made from this stock solution to 10, 100, 1000, 10,000 and 100,000 times dilutions. The corresponding thicknesses can be found in Table 18.

0.5 mL of the sample was carefully transferred to the Petri dish with a glass micropipette on the inner side of the dish, to make sure that the sample positioned on the seawater surface. The set-up was left for at least 5 minutes to allow for the DCM to evaporate completely and the oil to spread. 1.0 and 1.5 μL of ThickSlick 6535 and OP-40, respectively, were applied directly to the seawater surface to contract the oil, this corresponds to approximately a dosage of 150 $\mu\text{l}/\text{m}^2$. Surplus herder was observed as droplets.

The exposure procedure was as described above.

5.5.1.2.5 Controls

Control experiments with only 30% seawater were made.

Control experiment with 0.5 mL DCM carefully transferred to the Petri dish with a glass micropipette on the inner side of the dish, to make sure that the sample positioned on the seawater surface.

The exposure procedure was as prescribed above.

5.5.1.3 Barbule amalgamation index

The ‘barbule amalgamation index’ (AI) is a method developed to quantify the clumping of barbules as a result of exposure to oil by O’Hara and Moradin (2010). The clumping of the barbules, relates to the capacity of the feather to repel water, which is dependent on the ratio of barb thickness and distance between barbs, among other things (Stephenson 1997). The same method was used in our experiments for evaluation of the effect on the feather microstructure from the different exposure tests.

On each feather sections of approximately 25 proximal barbules were measured (see Figure 82 for terminology details). In each section the numbers of proximal barbules in each clump were counted and the AI was calculated for each section as mean barbules per clump. This was done for three barbs on each photo (See Figure 82) resulting in 12 AI for each feather. Examples of how AI was calculated are given in Table 19.

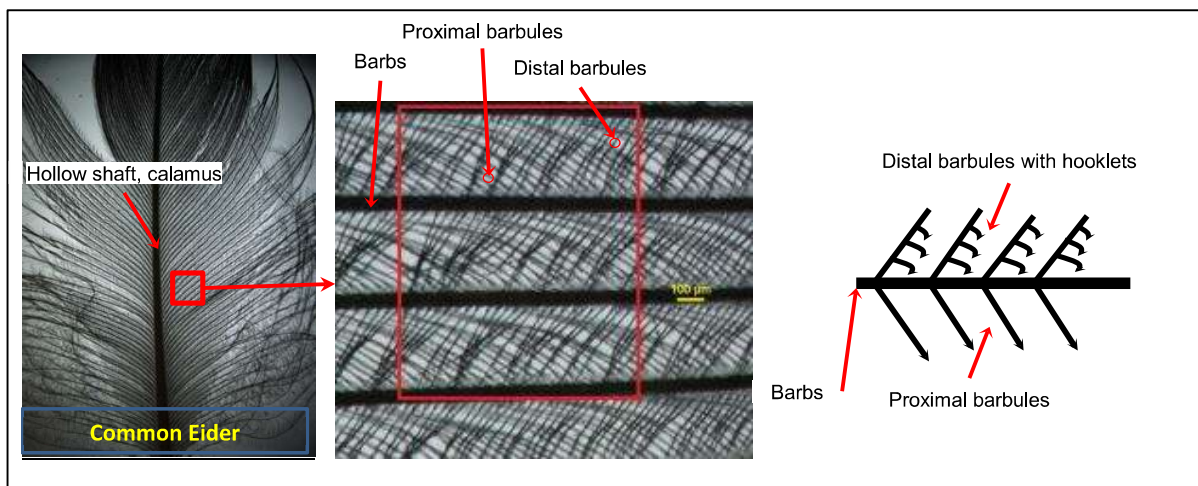


Figure 82: Bird feather terminology.

Table 19: Examples of AI for Thick-billed Murre for seawater, burn residue (1.07 μm) and ThickSlick6535 exposure.

Sample ID	No. Proximal barbules	Proximal barbules in each clump	AI = $\frac{\sum(\text{barbules})}{\sum(\text{clumps})}$
Seawater	26	3 1 3 2 1 1 1 2 2 1 1 2 1 1 1 3	1.63
ANS-OP-Res x10 (1.07μm)	25	3 2 20	8.33
TS6535	24	5 5 2 7 5	4.80

5.5.1.4 *Data treatment*

The AI of each feather was calculated as the mean of the AI count on the three photos on which four locations were counted. A test of differences in mean AI index among controls and herders, Bartlett's test of homogeneity of variances, was applied. This test showed that variances were not homogeneous ($p < 0.001$) both in the case of Eider and Thick-billed Murre, and demonstrated that transformation of the data or use of a non-parametric test were needed. Rank transformations generally works well with experimental design (Conover, 1999), therefore the mean AI indices were rank transformed prior to performing an analyses of variance (ANOVA). Tukey's *post hoc* test with a significant level of 5% was applied to tests of pairwise differences in mean AI.

The effects of dilution degree on AI were estimated by weighted (1/SD) linear regression of mean feather AI index on log-10 transformed dilution factor. Ordinary linear regressions were performed when evaluating the effect of dilutions degree on feather weight increase. Statistical analyses were done by using the software R version 3.1.3 (R Core Team, 2015).

5.5.2 *Results*

The results covers visual observations, feather weight changes and effects on the feather microstructure. The latter is only assessed for the application dosage (C) experiments and experiments including oil/residue.

5.5.2.1 *Visual observations*

The OP-40 monolayer experiments (A) showed that the feathers absorb water. This was the same for both bird species. 1-2 ANS crude oil droplets was applied after approximately 1½ hours and the herder had little effect on the oil slick and after ½ h the oil could only be seen as sheen. A second OP-40 monolayer experiment showed that after approximately 20 minutes the herder could keep the oil droplets contracted for 1 hour: thereafter the oil spread out as sheen.

It was seen for the minimum effective dose experiments (B) that for OP-40 the feathers sank completely after a few seconds. For the last experiment in the OP-40 baking tray the sinking was however not as fast as the other experiments. This is considered to be a result of the long time since the application of the herder. At the end of all the experiments 1-2 droplets of ANS crude oil was applied to see if the herder could still contract the oil. The OP-40 minimum effective thickness experiments could keep the droplets of ANS contained for more than an hour, thereafter the experiment were ended.

The TS6535 monolayer (A) and minimum effective thickness (B) dose experiments showed that the feather absorbs water, but remains on the water surface. The application of droplets of ANS crude oil showed that both herder doses contained the oil for more than an hour. After this the experiments were ended.

For the application dosage (C) experiments the feather also sank immediately (< seconds) after it was in contact with the herder OP-40. For the TS6535 experiments the feather was slowly (> minutes) soaked with water.

5.5.2.2 *Changes in feather weight*

The weights of the feathers were measured before and after the exposure and the changes in the weights due to absorption of water, DCM, oil/residue and/or herders are given in Figure 83 and Figure 84 for the Common Eider and Thick-Billed Murre. The weights are given as the average

change in weight for the triplicate experiments. The category ‘controls’ includes seawater and DCM and consists of up to 11 exposure experiments.

The weight increases of the experiments were analysed by an analyse of variance (ANOVA) followed by Tukey’s *post hoc* test for pairwise comparisons which is illustrated in Table 20. The weight increases for both bird species are significantly higher for the herders than for seawater as well as DCM. The weight increase is largest for the minimum effective thickness dose exposure experiments (B) and largest for the OP-40 experiments with Common Eider feathers. The smallest weight increases were found for the monolayer dose experiments (C), in particular for TS6535. It should be noted that the variation within the experiments were rather high which results in relatively few statistical significantly differences. Thus, even though the feathers did not sink as a result of the exposure to monolayers of herders (A), effects on the feather are still found (weight increase) due to entrainment of water into the feather microstructure. For both Eider and Thick-billed Murre no significant difference were found between seawater and DCM.

Table 20: Results of Tukey’s *post hoc* test of pairwise comparisons. Experiments are listed in decreasing order of weight increases. Experiments underlined are not significantly different at the 5% level.

	OP40 -B	TS - B	TS - A	OP40 - C	OP40 - A	TS -C	DCM	Seawater
Thick-billed Murre	_____							

Common Eider	_____							

For the exposure experiments using only crude oil and residues, the weight changes are at the control level for the 10 or 100 times diluted samples. The changes in feather weight for the highest oil and ANS burn residue concentration exposure experiments are comparable with the weight increases seen for the herder exposure experiments.

For the combined herder (application dose rate (C)) and crude oil exposure experiments the weight difference is considerably higher. Even at a dilution of 100,000 the weight differences are higher than the control. This is considered to be due to the presence of the herder and the derived effects. The trend seems similar for the two bird species, however the weight differences appear higher for Common Eider than Thick-billed Murre for all dilutions. The weight change data indicate a cumulative effect from the combined herder and oil experiments, likely caused by the presence of the herder that result in an increased water uptake.

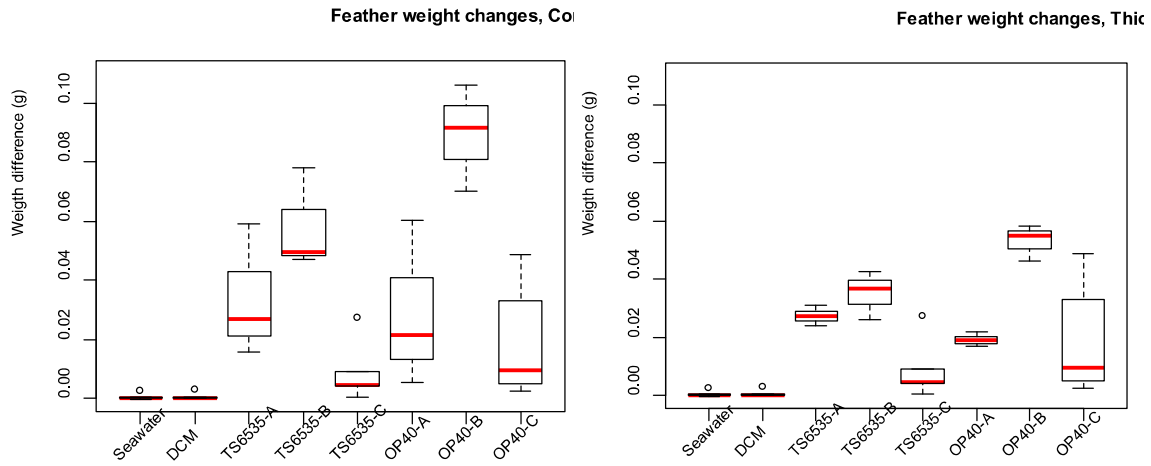
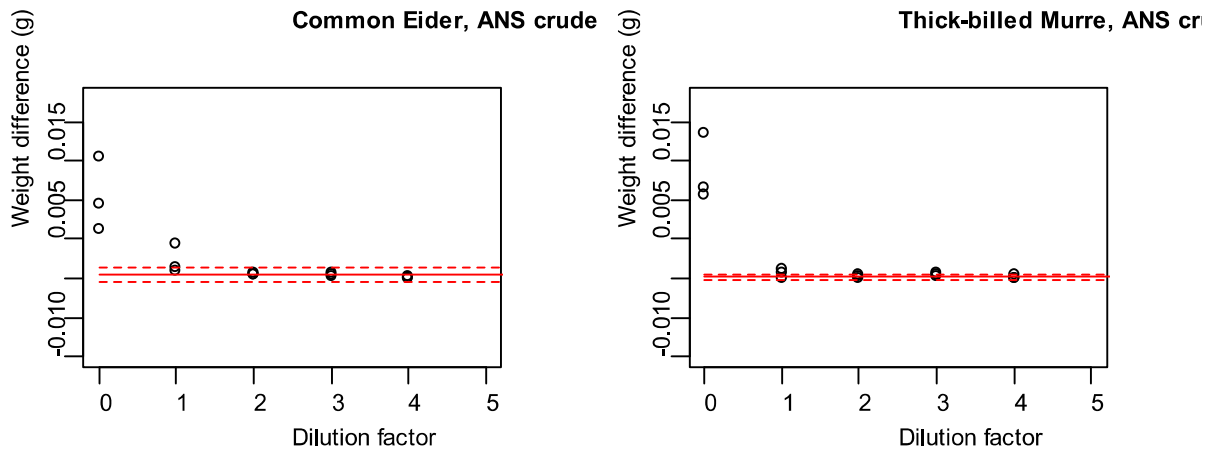
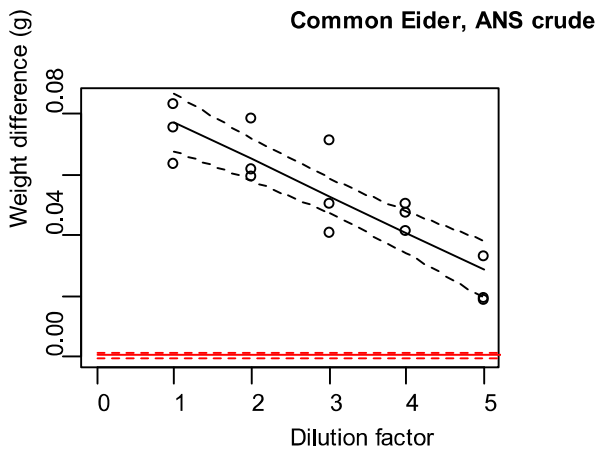
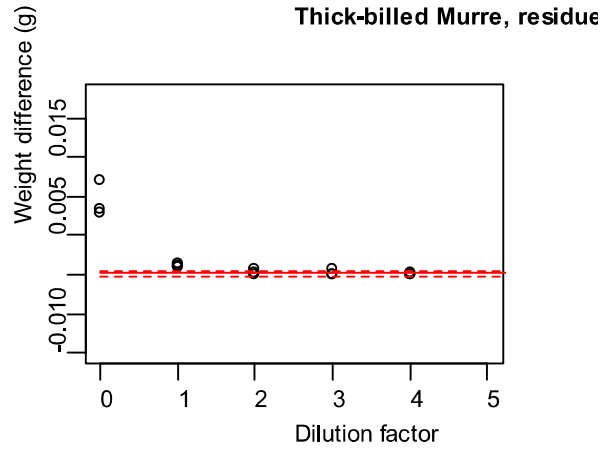


Figure 83 Boxplot of feather weight changes. Red lines represent medians, the bottom and top of the box show the 25th and 75th percentiles, the vertical dashed lines show the smallest of maximum and minimum or 1.5 times the interquartile range (roughly 2 SD) and the points shown are considered as outliers (more than 2 SD).





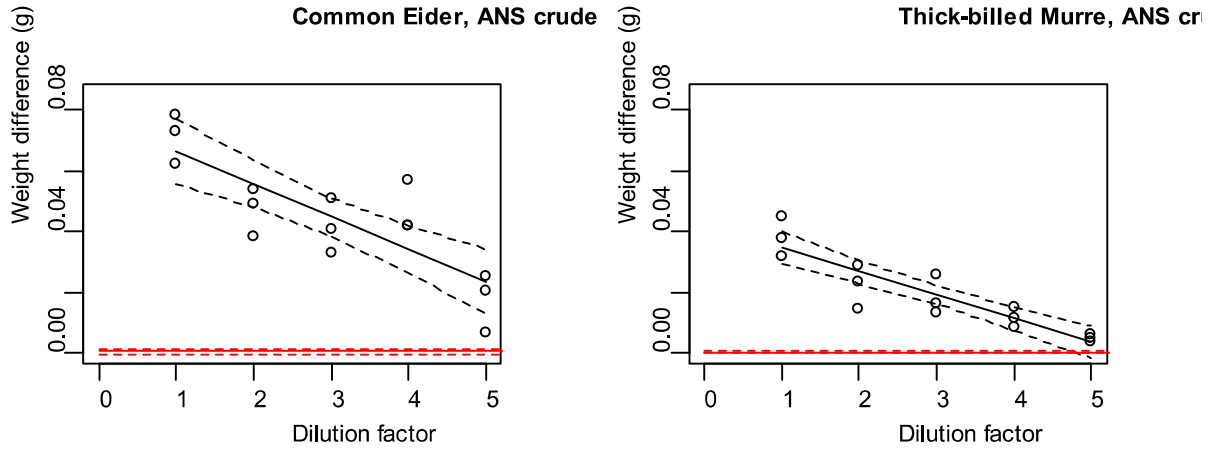


Figure 84: Weight change of each feather (three feathers for each dilution) versus \log_{10} of the dilution. Black lines represent regression lines of weight difference on dilution factor and black broken lines the 95% confidence for the regression. Red lines represent the mean of the seawater control and broken red lines 95% confidence limits of the mean. The dilution factor is based on \log_{10} transformed dilution, e.g. 1 on the x-axis corresponds to 10 times dilution.

5.5.2.3 *Effects on feather microstructure*

The effects on the feather microstructure are assessed by use of the AI for the application dosage rate (C) exposure experiments. In few cases the feather was completely smeared in oil that did not allow for counting the proximal barbules or calculating the AI (an example is given in Figure 85). In those cases the AI was set to 25, which is the maximum AI possible. Examples of images for the different categories of exposures are shown in Figure 86 and 87 for Common Eider and Thick-Billed Murre. All the herder dose rates used in these examples are the application dose rate (C).



Figure 85: Example of a feather heavily smeared in oil, thus AI is set to 25. Thick-billed Murre exposed to TS6535 and ANS (1.16 μm ; estimated sample thickness based on the assumption that the oil sample was homogeneously distributed over the test surface area, however note that the oil was herder and probably much thicker).

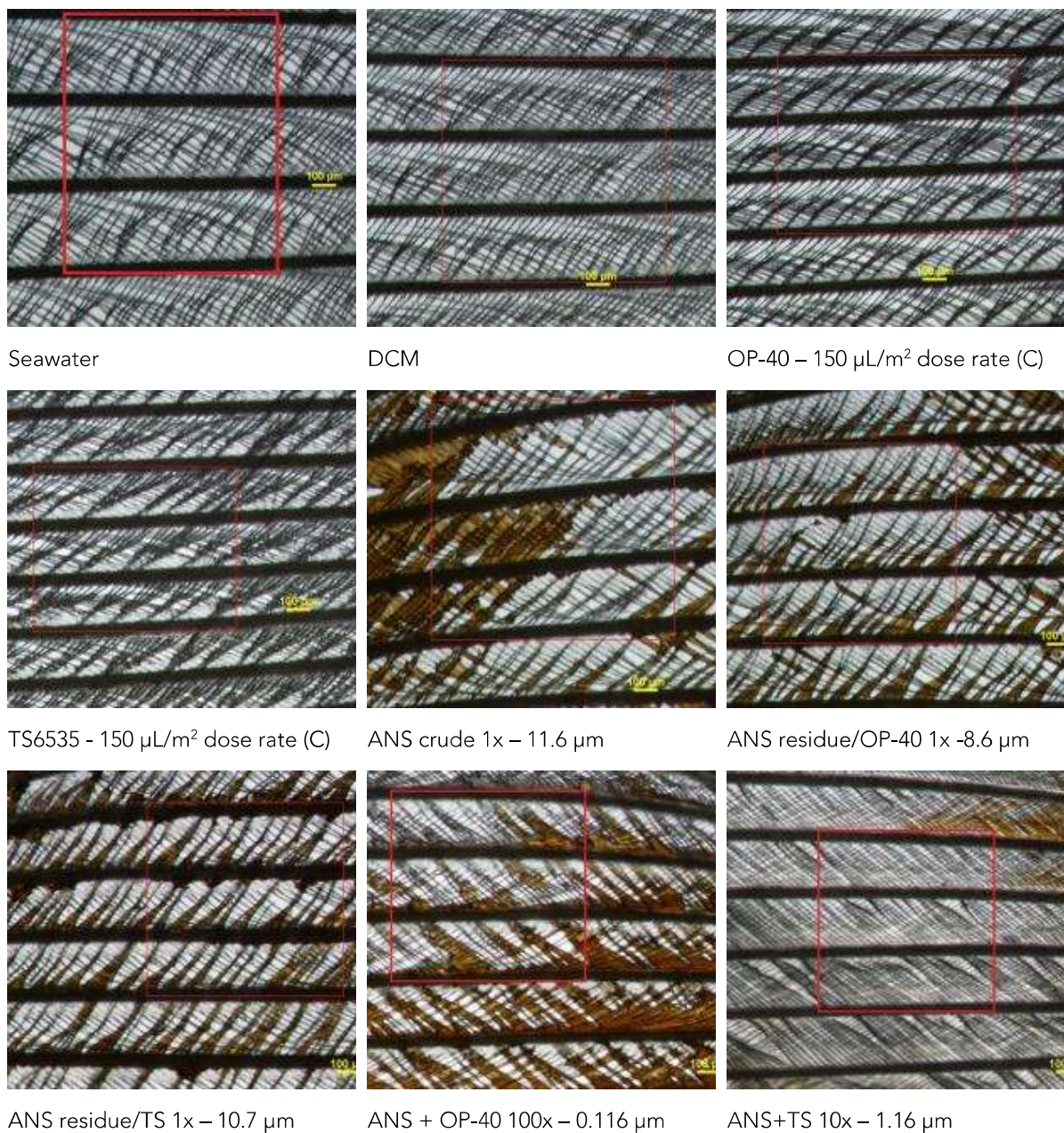


Figure 86: Images of Common Eider feathers at 11.25x magnification showing barbs (thick) and barbules (thinner lines) after exposure to herder, residue, crude oil and controls (seawater and DCM). The thicknesses given are the oil/residue film thicknesses estimated based on the assumption that the oil/residue was homogeneously distributed over the test water surface area.

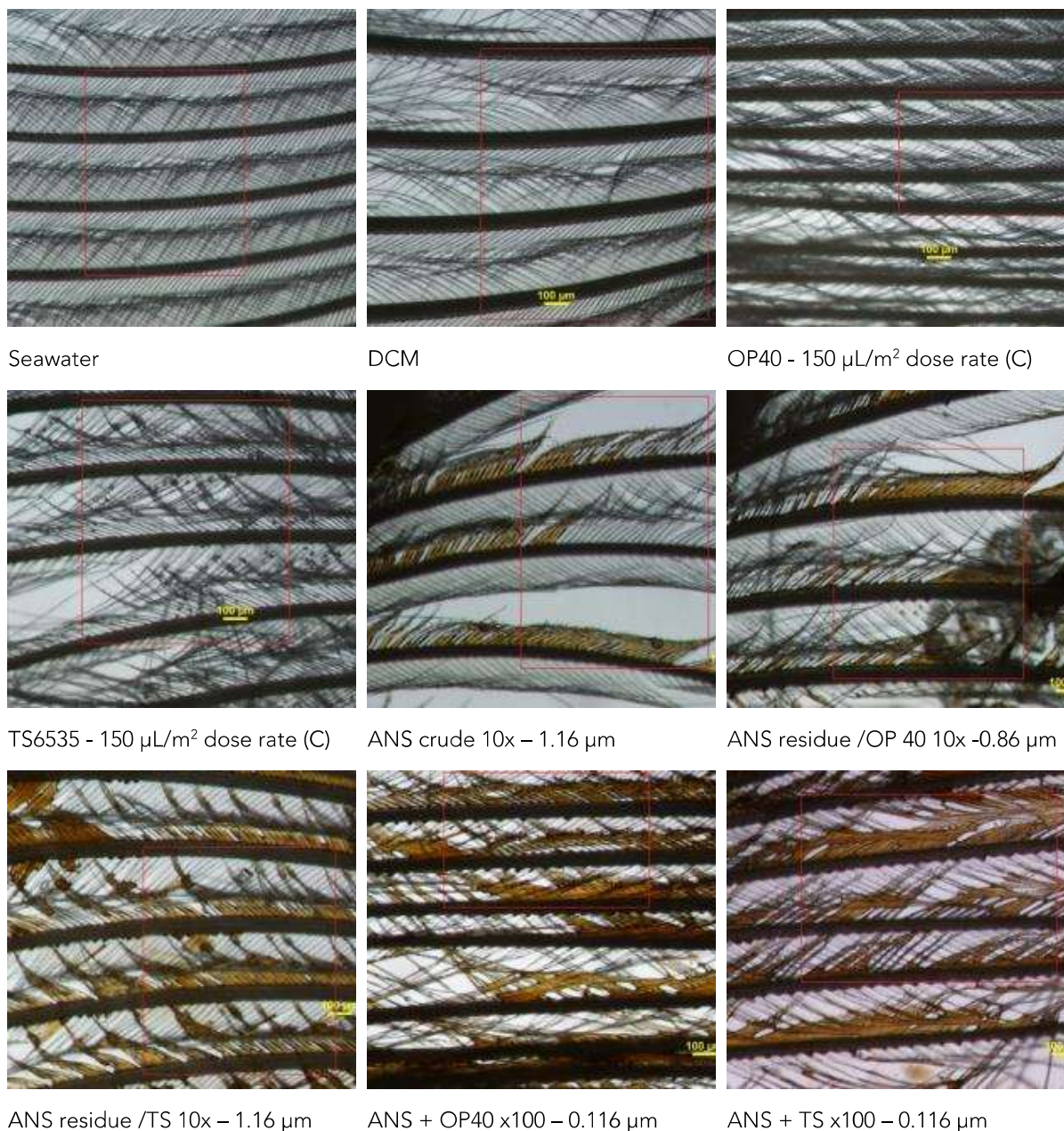


Figure 87: Images of Thick-Billed Murre feathers at 11.25x magnification showing barbs (thick) and barbules (thinner lines) after exposure to herder, residue, crude oil and controls (seawater and DCM). The thicknesses given are the oil/residue film thicknesses estimated based on the assumption that the oil/residue was homogeneously distributed over the test water surface area.

Figure 88 shows two boxplots of the AI for no exposure, seawater, DCM and the two herders for both Common Eider and Thick-billed Murre. In case of Common Eider, no significant differences were found among the AI for non-exposed, seawater and DCM. Similarly for Thick-billed Murre no difference was found between the seawater and DCM. For both Common Eider and Thick-billed Murre, there is no significant difference between the AI for TS6535 and OP-40. However,

TS6535 and OP-40 are both significantly different from the no exposure, seawater and DCM controls.

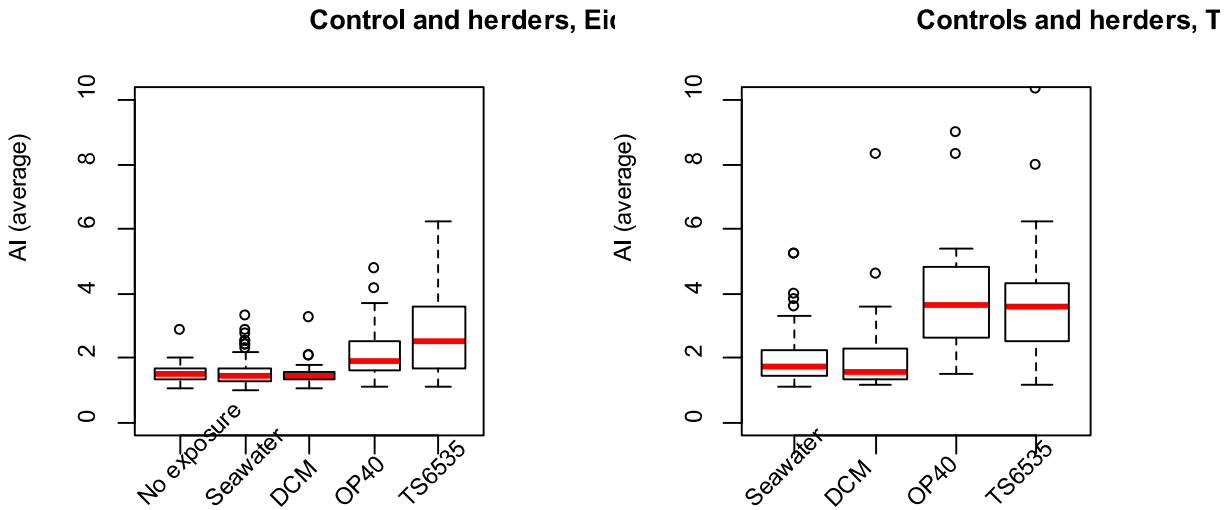
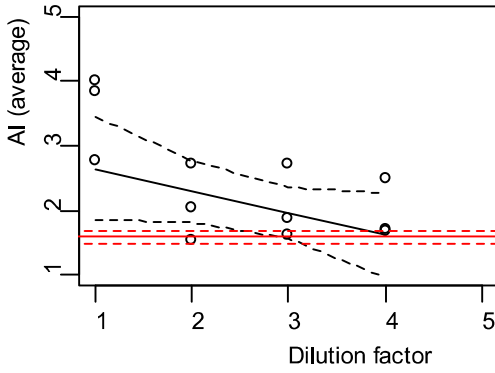


Figure 88: Boxplot of feather AI. Red lines represent medians, the bottom and top of the box show the 25th and 75th percentiles, the vertical dashed lines show the smallest of maximum and minimum or 1.5 times the interquartile range (roughly 2 SD) and the points showed are defined as outliers (more than 2 SD).

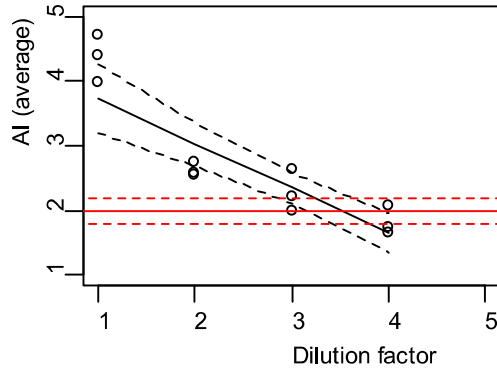
Figure 89 shows boxplots of the average AI for each exposure experiment (crude ANS, Residue/OP-40, residue/TS6535 and crude ANS + OP-40 and crude ANS+TS6535). The AIs for the lowest dilutions (highest dose/concentrations) are not shown in the boxplots, as these AIs were around 25.

For most of the exposure experiments the AI decreases by increasing dilution factor (decreasing concentration), however the negative regression lines are not significant ($p > 0.05$) for Eider ANS crude, Eider and Thick-billed Murre ANS + OP-40 and Eider and Thick-billed Murre ANS + TS. For all other exposure experiments the regression lines are declining ($p < 0.05$).

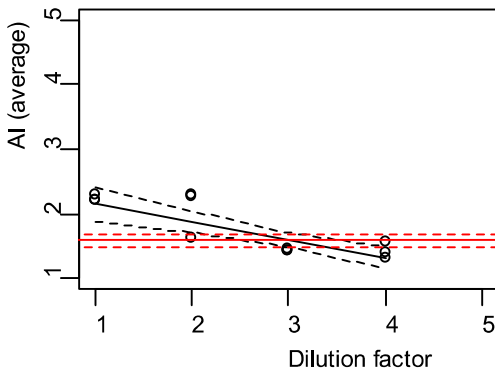
Common Eider, ANS Crude



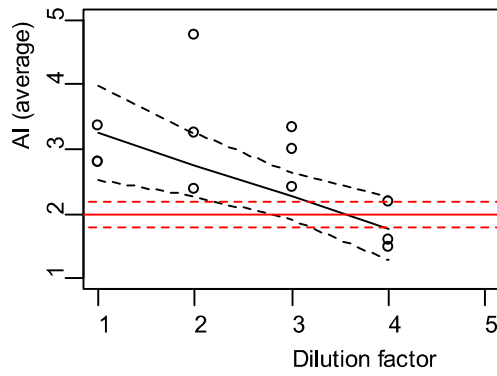
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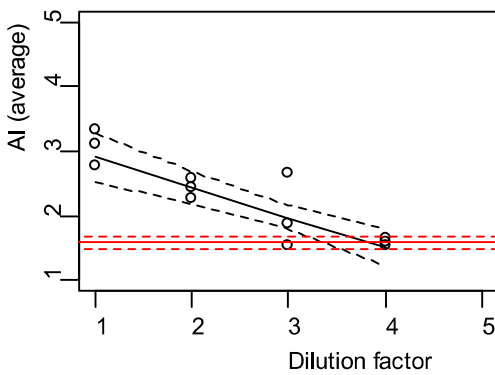
Common Eider, residue/TS



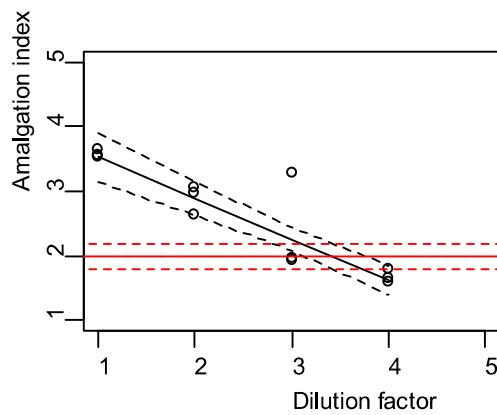
Thick-billed Murre, residue



Common Eider, residue/OF



Thick-billed Murre, residue



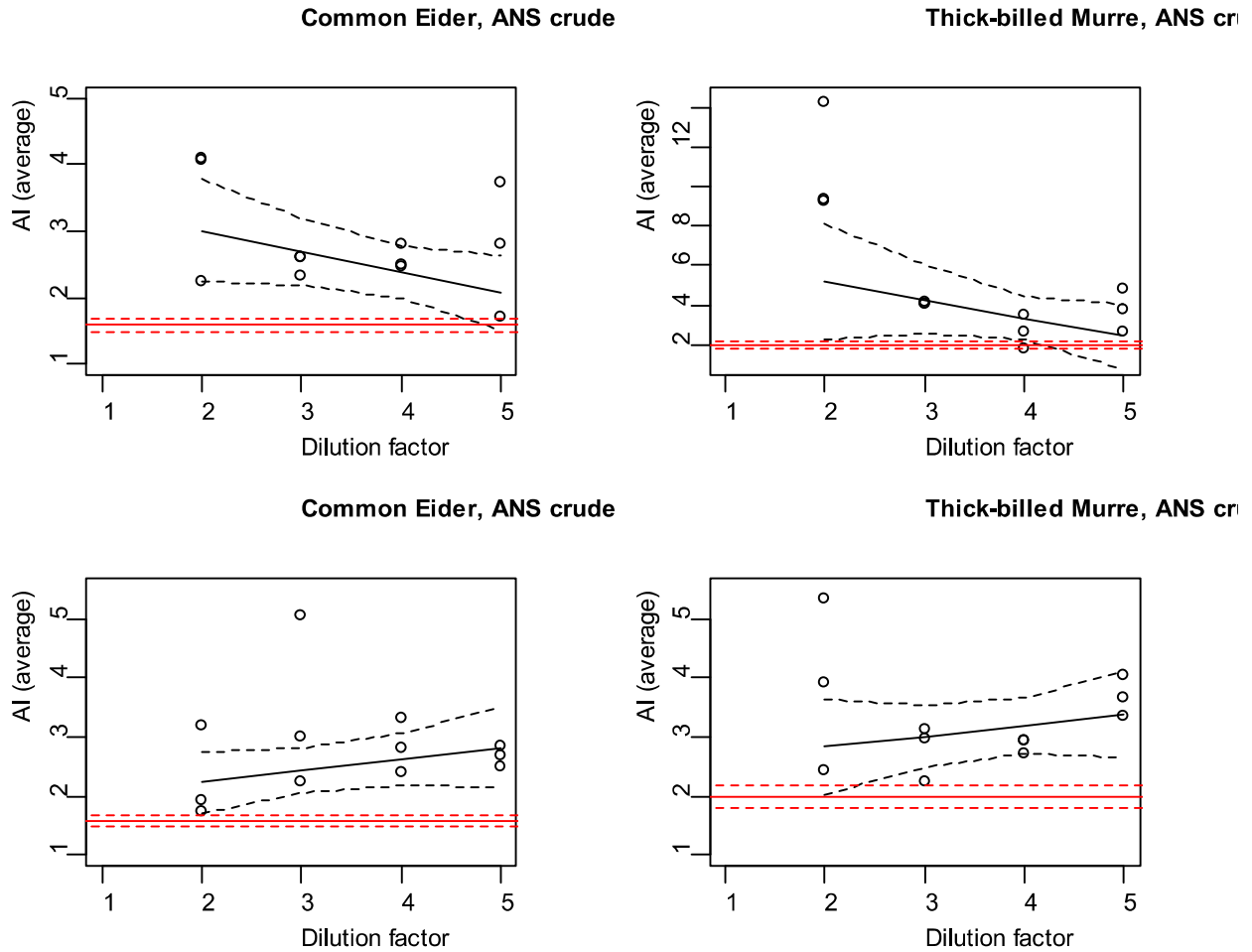


Figure 89: Average of AI of each feather (each feather having 3 photos on which 4 locations are counted) versus \log_{10} of the dilution. Black lines represent weighted (1/SD) regression lines of and black broken lines the 95% confidence for the regression. Red lines represent the mean of the seawater control and broken red lines 95% confidence limits of the mean. The dilution factor is based on \log_{10} transformed dilution, e.g. 1 on the x-axis corresponds to 10 times dilution.

The film thickness has been estimated by use of the known amount of oil/residue applied to the petri dish. Also a No Observed Effect Concentration (NOEC) has been identified from intersects between regression lines and the mean of the seawater control (in Figure 82) and the related No Observed Effect Slick Thickness (NOEST) was calculated. The results are shown in Table 21. There is a slightly tendency that Common Eider feathers are more sensitive than Thick-billed Murre feathers. Also there is a tendency that the combined experiments with both crude oil and OP-40 results in the lowest effect thicknesses. No NOEC or NOEFT are given for the ANS+TS6535, due to the fact that there was no point of intersection between the regression lines and the mean of the seawater control. This is considered to be a result of the presence of the herder in the experiment and the impact on the feathers regardless of the concentration of the oil. In spite of the experimental variations, the results give no indication of an increased effect seen by the combined oil/herder impact.

For the herder exposure experiments only one concentration was used; the application dosage rate of approximately $150 \mu\text{L}/\text{m}^2$ and it was observed that this concentration had an effect on the

feather microstructure. This concentration is expected to give a herder thickness of 0.15 μm , but a surplus of herder was observed as droplets on the water surface. Thus, the actual thickness is expected to be smaller, most likely monolayer thickness, but with access to some kind of reservoirs of herder to replace losses from the film, due to e.g. absorption in the feather structure.

Table 21: Estimated film thickness for max dosage, No Observed Effect Concentration (NOEC) and No Observed Effect Slick Thickness (NOEST).

	Experimental ID	Estimated film thickness for max dosage*) [μm]	NOEC [g/cm^2]	NOEST **) [μm]
Common Eider	ANS crude	11.6	8.04E-08	8.99E-04
	residue/OP-40	8.6	1.17E-07	1.27E-03
	residue/TS	10.7	8.80E-07	9.56E-03
	ANS + OP	11.6	2.66E-10	2.98E-06
	ANS + TS	11.6	-	-
Thick-billed Murre	ANS crude	11.6	3.27E-07	3.66E-03
	residue/OP-40	8.6	3.15E-07	3.42E-03
	residue/TS	10.7	2.85E-07	3.09E-03
	ANS + OP	11.6	3.94E-09	4.40E-05
	ANS + TS	11.6	-	-

*) calculated average thickness based on that the oil/residue/herder was homogeneously distributed over the water surface

**) estimated average thickness if the oil/residue/herder was homogeneously distributed over the water surface

5.5.3 Discussions

The AI and weight change results for both bird species did not show any significant difference between the feather exposed to DCM or seawater. This shows that DCM will not affect the feather structure or weight compared to only seawater exposure, and as expected DCM, is suitable as a solvent for these experiments. It is however important that enough time for the DCM to evaporate is allowed before the actual feather exposure experiments, to see the actual impact from the oil/residue/herder.

The results also showed that Common Eider feathers appeared slightly more sensitive than Thick-billed Murre feathers. A study by Jenssen and Ekker (1991) also showed that there is interspecies variation in sensitivity to oil and this could be explained by plumage structure where the soft and air-filled plumage of the Common Eider is expected to more easily collapse.

Both herders did result in significant increase in the feather weight (dosage A, B and C experiments) and AI (dosage C experiments) compared to seawater. Another observation was that for the highest dosages (B and C) the feather sank immediately (< seconds) after it was in contact with the herder OP-40 (see Figure 85). This was not the case for the monolayer dosage

(A). It is expected that the monolayer thickness will be the dominant thickness of the herder area, but that the thickness of the herder will range from a monolayer (10 Å to 30 Å) to the application dose thickness (0.15 µm or 1500 Å) or even higher where the excess herder droplets is found, until the herder has completely spread out to a monolayer. For the all TS6535 experiments the feather was slowly (> minutes) soaked with water. The high weight gain for all the herder experiments (all dosages) strengthens these observations.

The capacity of a feather to repel water is dependent on the ratio of barb thickness and distance between barbs and the surface tension of the water (Rijke 1968). Exposure to oil might lead to the microstructure of the feather being disrupted with the result that hooks, barbs and barbules collapse. Such collapses will change the ratio of barb thickness and distance between barbs so much that the surface tension of the water will no longer prevent water penetration (O'Hara and Morandin 2010). Surface tension is in other words the force that resists infiltration of water into the plumage (Stephenson 1997). According to Stephenson (1997) the critical surface tension for feather wetting is conservatively estimated to be in the range of 38-50 mN/m. Normal seawater surface tension is on the order of 70 mN/m. Stephenson (1997) also suggested that the feathers might lose their water repellence with minor reductions in the surface tension, due to the fact that it is the surface tension that is the force that resist the passage of water through the pores. According to SLRoss and DCE (2015) herders will reduce the surface tension of the surrounding seawater water to 20-30 mN/m, which is well below the critical surface tension for feather wetting given by Stephenson (1997). The theory thus supports the laboratory findings of the sinking of the feather for OP-40 and water absorption for TS6535.

From the findings of the experiments and knowledge about the behaviour of the seabirds described above, it seems likely that a seabird exposed to a monolayer of chemical herders will become wet as the reduced surface tension will allow the water to penetrate into the plumage, both in between the feathers and also through the microstructure of the feather. This will result in the loss of insulation of the feather plumage. When this air layer in the plumage is lost either by displacement by oil or water it might let to hypothermia (Stephenson and Andrews 1997).

Based on our experiments it is difficult to deduce anything about the reversibility of the wetting of the feathers. However, from Lambert et al. (1982) it was found that for birds exposed to dispersants, the birds remained wet for much longer than for birds only exposed to water or even oil (Lambert et al. 1982). Jenssen (1994) concludes in a review article based on findings from cleaning of oiled birds that it is possibly to regain the water-repellent and insulation function of the plumage when all oil and detergent are removed and the plumage is completely dry. Other results indicate however that rehabilitated birds are more sensitive to recontamination (Jenssen 1994). From monitoring of de-oiled and released penguins in South Africa the results showed that the penguins had the same survival rate and breeding success as non-impacted penguins (Wolfaardt et al. 2008). On the other hand de-oiling experiences from other parts of the world (e.g. Exxon Valdez) are less encouraging and the conditions of rehabilitated birds are generally poor. Thus, to fully understand the effects in long term from herders on seabirds more studies are needed.

5.5.4 Conclusions

- For most of the exposure experiments the AI decreases with decreasing concentration.
- No Observed Effect Concentration (NOEC) and the related No Observed Effect Slick Thickness (NOEST) was calculated. Thick-billed Murre seems less sensitive than Common

Eider in the combined experiments with both crude oil and OP-40 results in the lowest effect thicknesses.

- Both herders significantly increase the feather weight and Amalgamation Index (AI).
- The OP-40 monolayer experiments (A) showed that the feather absorbed water, but did not sink. The feathers exposed to higher dosages (B and C) sank immediately (< seconds) after it came in contact with herder.
- The feathers exposed to all three dosages (A, B and C) did not sink, but slowly absorbed water.
- It is expected that the monolayer thickness will be the dominant thickness of the herder area, but that the thickness of the herder will range from a monolayer (10 Å to 30 Å) to the application dose thickness (0.15 µm or 1500 Å) or even higher where the excess herder droplets is found, until the herder has completely spread out to a monolayer.

5.6 Smoke Plume Analysis

5.6.1 Introduction

When applied as intended, herding agents spread rapidly into very thin layers in contact with the edge of an oil slick. In general, the ultimate thickness of the herder will range from a monolayer (10 Å to 30 Å) to the application dose thickness (0.15 µm or 1500 Å). Considering that:

- The measured Flash Points of the herders are >85 °C for TS6535 and > 100 °C for OP-40;
- The minimum ignitable thickness for oil on water is approximately 1 mm (10⁶ µ); and,
- The herders form a transparent film on the water surface

it is difficult to imagine how the adjacent crude oil fire could ever heat the very thin film of herder to a point above the ambient water temperature, let alone to its Flash Point, in order to ignite the herder film. From the estimates of resultant herder concentrations in the burn residue (Figure 69), there may be low concentrations of herders (roughly 1000 ppm OP-40 or 10,000 ppm TS6535) present. Unintentional overspray on to part of the oil slick, or dissolution of the herders into the oil before or during ISB could possibly be a source of herder combustion, leading to combustion products in the smoke plume. Dissolution concentrations would be dependent upon the time lag between the application of herding agents, and the combustion of the oil slick. Any small amounts of evaporated herder would be drawn into the adjacent fire premixed with combustion air, which should ensure complete combustion.

Nevertheless, a series of experiments were conducted in the spring and summer of 2015 at the SL Ross Laboratory in Ottawa in support of the Herder Fate and Effects portion of the study.

5.6.2 Goal

The goal of these experiments was to determine whether combustion products of the two commercially-available herders (ThickSlick 6535 and OP 40) used to contract slicks of oils to ignitable thicknesses would end up in the smoke generated by burning the oil slick. Once ignited, the smoke plume would be sampled to determine if the herder or herder combustion products could be detected. The experiments involved two fresh crude oils and one crude that had been quantitatively evaporated (weathered).

5.6.3 Methodology

The crude oil for the experiments was artificially evaporated by sparging compressed air into pre-weighed 20L cans of the oils. The cans were weighed periodically to measure progress. As the mass loss slowed, electric band heaters were attached to the outside of the cans to accelerate evaporation of the oil. The target evaporative losses were based on earlier spill-related property studies of the crudes used in the experiments.

The oil and herder combinations in the SL Ross wind/wave tank were selected based on the results of the 1-m² and 10-m² Herder Pan Test (HPT) experiments.

For the ISB experiments, metal heat shields were installed along the sides of the tank and the metal fume hood was swung over the burn area. The smoke from the burns was removed with a 200-m³/min fan, through a 60-cm metal duct that is connected to the fume hood suspended approximately 1-m above the water surface.

A typical *in situ* burn experiment in the wind/wave tank involved the following steps:

1. Insert barriers at either end of the heat shielded test section and thoroughly clean the water surface with sorbent pads to remove any oil or herder traces.
2. Take a sample of the water from the surface using a Petri dish and measure the water-air interfacial tension (IFT) using the DuNuoy Ring Tensiometer. If the IFT reading is less than 60, reclean the test area.
3. A volume of 400 mL (to form an approximately 40-cm diameter herded slick) of fresh crude oil is measured into a graduated cylinder and weighed.
4. Place a sign at the edge of the tank that will be visible in the video denoting test number, conditions and approximate test time of day.
5. For those experiments involving pre-treatment of the water surface of the tank, 500 μ L of the herder is placed on the water surface using a micropipette.
6. The oil is carefully poured onto the surface of the tank.
7. Ignition is attempted first with a propane soldering torch flame.
8. A stopwatch and video records the following times: initial ignition time, 50% flame coverage of slick; full ignition (100% flame coverage); time to the vigorous (or intense) burn phase; 50% flame extinction; and, extinction.
9. The smoke plume is sampled approximately 30 seconds after full ignition, for a duration of 20-30 seconds.
10. After extinction of the flame, pre-weighed rectangles of sorbent are used to recover the residue from the water surface. After use, each pad is shaken to remove as much water as possible. Then the pads were reweighed to determine the mass of residue. The sorbent pads are then hung up to dry overnight, and reweighed after any water had evaporated. It is assumed that very little of the burn residue evaporates in the same time period.

5.6.4 Test Oils

Two crude oils were selected for these tests:

- Alaska North Slope pipeline crude (sample obtained from a refinery in California in 2013)
- Grane crude from a platform off Norway in 2014.

Properties of the oils can be found in Table 1

5.6.5 Test Herders

Two herders, approved for listing on the U.S. National Contingency Plan Product Schedule, were selected for this programme:

- ThickSlick 6535; and,
- OP-40

Properties of the two herders can be found in Table 2.

5.6.6 Experiments

A total of eight burn experiments were sampled. Six burn experiments with the two herders (OP-40 and Thickslick 6535) and two parent oils (ANS and GRANE) were performed (see 90), along with two baseline tests which used a 40-cm diameter floating metal ring to contain the oil during the burns (see Figure 91). A matrix of the burns can be found below in Table 22.

Table 22: Experimental Matrix

<i>Burn Run</i>	<i>Air sample canister</i>	<i>Canister sample label</i>	<i>Herder Containment</i>	<i>Oil Sample</i>
0	#4893	HerdINV001	n/a	n/a
1	#4876	HerdINV002	Thickslick 6535	ANS fresh oil
2	#3659	HerdINV003	OP-40	ANS fresh oil
3	#4866	HerdINV004	OP-40	ANS 2 day weathered
4	#3703	HerdINV005	OP-40	ANS 14 day weathered
5	#3707	HerdINV006	OP-40	GRANE fresh oil
6	#3715	HerdINV007	Thickslick 6535	GRANE fresh oil
7	#3710	HerdINV008	mechanical ring	GRANE fresh oil
8	#3713	HerdINV009	mechanical ring	ANS fresh oil



Figure 90: Herded oil burning



Figure 91: Mechanically contained oil burning

Multiple 4 litre air sampling canisters were used to sample smoke plumes. Stainless extension rods along with filters were used to allow sampling to be performed at a safe distance, and to limit any large particles that may be drawn into the canisters during the sampling process (see Figure 92). Sampling times ranged between 20 to 30 seconds as the samples were drawn into each canister during the burns. Samples were then sent to Environment Canada's Air Quality

Research Division – Emissions Research and Measurement Section analytical laboratory for analysis. Their air quality research facility is located in Ottawa, Canada, and includes a state-of-the-art emissions testing laboratory capable of conducting detailed emissions measurements from a variety of mobile sources. The protocol they followed is their standard method used for the detection of combustion products when sampling exhaust stacks from the combustion of hydrocarbon based fuels. Details of ERMS Method 4.04 may be found in Appendix YY.



Figure 92: Sampling canisters

5.6.7 Results

The initial background sample, HERDINV001, was taken in the vicinity of the test tank while other experiments with crude oil were being conducted in the lab. Some of the analyzed compounds had higher than expected results but when other activities occurring in the lab were taken into account, the numbers make sense (see Table 24). These same tests were ongoing during the subsequent smoke plume sampling as well.

The analysis focusses on VOCs and is tailored to identifying multiple compounds that are not typically of interest – but have been identified here for completeness as they form part of Environment Canada’s standard analysis for emissions from mobile sources. The results shown below in Table 3 demonstrate that the use of either herder did not have a negative impact on the primary BTEX compounds. In fact, when comparing the mechanical containment results (HERDINV008 and HERDINV009), the analytical results of BTEX are generally improved with the herder retained burns (HERDINV002 through HERDINV007). In addition, the chromatograms did not show any obvious signs of the herder being present. These preliminary screening tests indicate there is no significant increase in the products of combustion in the smoke from a herded slick.

The analyst did note that the HERDINV008 run had a very large interference and compounds from 2-butyne through cyclopentene could not be reported with any great accuracy.

Supplementary testing was performed to provide additional baseline data on the analyses. A sample of each of the herders was placed in a Pyrex® container and subjected to flame impingement from a propane torch for an initial period of approximately 30 seconds, then air sampling was conducted from a stove pipe section held above the container for an additional 20 to 30 seconds while the propane torch continued impinging on the liquid (see Figure 93). The first run was an empty container, with Thickslick 6535 and OP-40 being used in the next two runs as shown below in Table 23.



Figure 93: Stack assembly used in Herder/Torch Impingement tests

Table 23: Herder Flame Impingement Analysis

Burn Run	Air sample canister	Canister label	sample Herder
9	#4875	HerdBase1	n/a
10	#5961	HerdBase2	Thickslick 6535
11	#5960	HerdBase3	OP-40

The results of the impingement tests show low VOCs (see Table 25). The first test in this series, HerdBase1 showed very low concentrations of most compounds with the exception of propane – which was the source of combustion as a propane torch was impinging on the Pyrex® container. There were comparatively low concentrations of low molecular weight VOCs produced when the pure Thickslick 6535 was subjected to flame impingement, but these concentrations pale in comparison to the concentrations of VOCs produced during the combustion of oil slicks. There were no measurable VOC's above the baseline when the flame impinged on the pure OP-40.

The overall conclusion from this testing is that the data showed no apparent incidences of herder in the smoke plumes, as expected. A comparison of the use of mechanical containment (metal ring) versus the application of a chemical herder around the perimeter of a spill actually showed a slight decrease in BTEX detected in the smoke plume when the chemical herders were used. No other noticeable differences on the impacts of combustion were noted between the two methods of containment.

Additional research is suggested, focussing specifically on the analysis of possible siloxanes being formed at very low concentrations during the combustion of oil contained by the OP-40 herder. Given the thinness of the herder film, its high flash point and transparent nature and the dilution effect of the relatively large amount of oil being combusted, specialized monitoring and/or analytical equipment would be needed to detect the presence of such compounds that were beyond the scope of this project.

Table 24: VOC Analysis Results

Volatile Organic Compounds [by GC-FID with cryogenic preconcentration, ERMS Method 4.04/*.* /M]

* Full VOC compound list - BOLD RED values surpass upper limit calibrations

MQL	Calibration Upper Limit (ng/L)	Test Type:	Canister #									
			4893	4876	3659	4866	3703	3707	3715	3710	3713	
			HERDINV001	HERDINV002	HERDINV003	HERDINV004	HERDINV005	HERDINV006	HERDINV007	HERDINV008	HERDINV009	
0.15	280	Ethylene	313	37906	8401	11893	1525	8136	28353	26780	33546	
0.22	260	Acetylene	38	26323	8574	13330	2141	12748	27003	54975	32533	
0.22	300	Ethane	579	1877	456	377	54	529	1262	25626	1170	
0.09	420	Propene	181	8120	1582	1675	210	748	4096	19269	4793	
0.14	440	Propane	336	941	572	57	33	302	178	389	502	
0.09	420	Propyne	397	1395	327	595	66	398	1190	4475	1459	
0.10	580	Isobutane	150	608	942	50	32	207	68	128	220	
0.12	513	Isobutene/1-Butene	108	2234	446	409	63	171	577	4595	1043	
0.19	623	1,3-Butadiene	11	38	6	16	1	45	1115	7838	502	
0.21	580	Butane	586	1830	3218	171	83	215	255	215	817	
0.08	560	trans-2-Butene	30	1062	83	493	56	378	851	422	727	
0.12	513	1-Butyne										
0.16	560	cis-2-butene	21	160	33	25	7	29	50	360	75	
0.19	623	1,2-Butadiene	0	60	12	16	2	13	46	218	56	
0.09	641	3-Methyl-1-butene	6	138	33	27	5	13	17	222	56	
0.24	660	2-Methylbutane	381	813	1935	133	82	236	99	137	397	
0.19	623	1,4-Pentadiene										
0.12	513	2-Butyne	1	44	8	11	1	8	36		37	
0.09	641	1-Pentene	8	545	122	114	23	34	45		215	
0.09	641	2-Methyl-1-butene	25	197	48	36	7	21	30		73	
0.11	660	Pentane	225	631	2073	146	100	103	42		355	
0.19	623	2-Methyl-1,3-butadiene	1	237	67	60	10	8	91		118	
0.22	641	trans-2-Pentene	25	102	34	18	4	16	16		35	
0.18	788	cis-2-Pentene	13	61	20	11	2	9	10		23	
0.09	641	2-Methyl-2-butene	131	137	104	10	6	1321	338		135	
0.19	623	trans-1,3-Pentadiene		3		1	1		32		1	
0.19	623	Cyclopentadiene		9	3	4	1	3	170		10	
0.18	788	2,2-Dimethylbutane/cis-1,3-pentadiene	12	30	66	7	4	13	20		16	
0.09	641	Cyclopentene	6	156	4	4	5	3	5		12	
0.25	770	4-Methyl-1-Pentene/3-Methyl-1-Pentene	3	248	47	44	6	15	23	20	94	

0.09	641	Cyclopentane	21	113	306	35	21	25	21	44	75
0.27	860	2,3-Dimethylbutane	48	104	196	25	17	33	18	124	47
0.10	860	2-Methylpentane	161	467	1250	150	94	95	53	97	281
0.25	770	cis/trans-4-Methyl-2-pentene	4	46	19	12	3	8	10	188	36
0.15	860	3-Methylpentane	142	340	764	89	58	58	28	285	168
0.25	770	2-Methyl-1-pentene	5	93	11	11	2	6	6		37
0.25	770	1-Hexene	3	780	172	169	25	47	66		349
0.25	860	Hexane	370	874	2030	249	156	66	33	640	423
0.25	770	trans-2-Hexene	17	78	33	21	5	11	13		22
0.25	770	2-Methyl-2-Pentene	10	102	29	20	4	13	16	52	22
0.25	770	trans-3-Methyl-2-Pentene	6	51	15	9	2	7	9	128	25
0.25	770	cis-2-Hexene	3	27	13	5	1	3	3	90	10
0.25	770	cis-3-Methyl-2-pentene	7	11	12	3	2	4	8	12	14
0.18	916	2,2-Dimethylpentane	2	4						64	
0.09	770	Methylcyclopentane	113	637	1141	191	104	113	62	211	274
0.18	916	2,4-Dimethylpentane	25	53	96	14	10	20	11	35	27
0.18	916	2,2,3-Trimethylbutane	2	11	11	3	1	5	11	10	17
0.09	714	Benzene	224	16882	6432	11341	1586	8067	22828	66018	26666
0.18	916	3,3-Dimethylpentane	29	155	26	45	7	19	97		88
0.18	840	Cyclohexane	36	502	1124	187	129	197	132		379
0.10	916	2-Methylhexane	38	253	448	85	54	109	43	72	162
0.38	916	2,3-Dimethylpentane	31	125	230	39	31	68	62	156	80
0.18	840	1,1-Dimethylcyclopentane	2	50	99	17	12	25	16	41	37
0.18	840	Cyclohexene	1	149	39	27	4	18	20	103	64
0.12	916	3-Methylhexane	51	450	609	123	76	149	73	263	270
0.18	840	cis-1,3-Dimethylcyclopentane	7	113	248	42	31	35	21	206	82
0.12	916	3-Ethylpentane/trans-1,3-Dimethylpentane	5	153	277	54	36	51	33	122	118
0.20	916	1-Heptene/trans-1,2-Dimethylcyclopentane	5	176	401	59	52	50	31	95	135
0.17	1045	2,2,4-Trimethylpentane	181	670	159	121	24	40	42	283	237
0.20	916	trans-3-Heptene	2	28	7	4	1	3	3	5	15
0.20	916	Heptane	38	577	1285	245	178	48	27	76	426
0.20	916	cis-2-Heptene	2		6	4	1	3	3	27	7
0.20	916	trans-2-Heptene	2	43	12	9	2	3	5	35	17
0.20	916	cis-3-Heptene	1	22	7	5	1	2	3	20	10
0.15	980	Methylcyclohexane/2,2-Dimethylhexane	28	1088	1743	347	254	344	238	1140	787
0.14	1045	2,5-Dimethylhexane/Ethylcyclopentane	25	146	205	41	31	18	11		91
0.14	1045	2,4-Dimethylhexane/2,2,3-Trimethylpentane	28	203	114	38	16	30	23	74	89
0.14	1045	3,3-Dimethylhexane/cis-trans-cis-1,2,4-Trimethylcyclopentane	4	89	119	28	20	22	14	80	61
0.15	980	cis-trans-cis-1,2,3-Trimethylcyclopentane	2	168	135	33	22	19	16	132	78
0.14	1045	2,3,4-Trimethylpentane	54	89	48	11	7	12	6		41
0.21	919	Toluene	1833	5711	2556	2126	434	1869	5651	185507	36802
0.14	1045	2,3-Dimethylhexane	17	84	64	18	11	14	10	111	41

0.14	1045	2-Methyl-3-Ethylpentane	2	96	62	18	11	16	10		26
0.10	950	2-Methylheptane/1-Methylcyclohexene	13	284	334	84	61	19	14		206
0.10	950	4-Methylheptane/3-Methyl-3-Ethylpentane	5	119	99	33	19	14	9	159	70
0.10	950	3,4-Dimethylhexane	4	64	33	13	6	10	7	58	32
0.12	1045	3-Methylheptane/3-Ethylhexane	16	247	260	68	48	27	16	77	161
0.15	980	cis-cis-trans-1,2,4-Trimethylcyclopentane/cis-1,3-Dimethylcyclohexane	23	523	362	107	63	84	61		299
0.15	980	trans-1,4-Dimethylcyclohexane	3	128	132	35	26	30	20	500	89
0.11	1045	2,2,5-Trimethylhexane	18	114	40	18	6	8	20	114	50
0.11	1045	1-Octene	2	326	104	75	18	19	23	243	159
0.15	980	1-Ethyl-1-methylcyclopentane	1	28	26	8	5	4	3	54	18
0.11	1045	Octane/trans-1,2-Dimethylcyclohexane	22	889	839	264	173	25	48	194	634
0.11	1045	trans-2-Octene	1	56	30	12	6	7	5	59	28
0.15	980	cis-cis-cis-1,2,3-Trimethylcyclopentane	4	100	76	23	14	20	13	65	64
0.11	1045	2,2,4-Trimethylhexane	1	45	24	8	4	6	6	46	25
0.11	1045	cis-2-Octene/Isopropylcyclopentane									
0.11	1045	2,3,5-Trimethylhexane	3	49	28	10	5	9	6	57	24
0.11	1045	2,4-Dimethylheptane	2	47	34	4	6	3	5	69	30
0.11	1045	2,6-Dimethylheptane/cis-1,2-Dimethylcyclohexane	2	52	50	20	10	6	13	98	39
0.15	980	n-Propylcyclopentane	7	340	263	93	52	86	56	66	257
0.15	980	cis-cis-cis-1,3,5-Trimethylcyclohexane	4	63	55	20	10	11	7	251	48
0.11	1045	2,5-Dimethylheptane/3,5-Dimethylheptane	671	856				70		83	
0.11	1045	3,3-Dimethylheptane			216	74	37	9	39	151	208
0.15	980	1,1,4-Trimethylcyclohexane	1	95	38	48	7	21	40	34	15
0.28	971	Ethylbenzene	168	655	257	160	52	163	217	763	452
0.15	980	cis-trans-trans-1,2,4-Trimethylcyclohexane	4	102	55	32	11	19	14	42	79
0.09	1280	2,3-Dimethylheptane	3	127	72	32	14	24	12	76	80
1.07	971	m&p-Xylene/3,4-Dimethylheptane	563	3092	1253	1648	330	1437	2618	6877	3837
0.09	1280	2-Methyloctane	10	278	154	81	34	17	11	37	202
0.09	1280	3-Methyloctane	9	222	117	65	26	13	16	54	162
1.30	857	Styrene/cis-trans-cis-1,2,4-Trimethylcyclohexane	9	283	90	145	19	213	2041	5500	1092
0.09	1280	3,3-Diethylpentane	2								
0.35	883	o-Xylene	177	634	210	155	41	145	216	751	459
0.09	1280	1-Nonene/1,1,2-Trimethylcyclohexane	7	158	73	41	15	34	21	112	115
0.09	1280	trans-3-Nonene	2	85	41	24	9	18	12	67	62
0.09	1280	cis-3-Nonene/Isobutylcyclopentane		53	23	17	6	17	13	66	47
0.09	1280	Nonane	28	830	346	233	84	32	18	47	601
0.09	1280	trans-2-Nonene	1	20	7	4	0			17	7
0.09	1280	cis-2-Nonene	8	202	66	46	13	34	26	129	120
0.28	1099	Isopropylbenzene	5	79	28	19	5	12	9	82	52
0.09	1280	2,2-Dimethyloctane	3	107	34	38	8	20	29	386	71
0.09	1280	Isopropylcyclohexane	8	235	85	57	19	54	36	200	160
0.09	1280	n-Butylcyclopentane	19	1221	409	632	74	225	710	1261	1115

0.09	1280	3,3-Dimethyloctane	7	55	19	13	5	19	11	59	34
0.47	1099	n-Propylbenzene	17	223	72	56	17	38	28	163	149
0.46	1099	3-Ethyltoluene	46	440	124	106	30	59	89	306	291
0.85	1099	4-Ethyltoluene/2,3-Dimethyloctane	32	264	78	63	20	55	48	199	188
0.52	1099	1,3,5-Trimethylbenzene	33	286	76	75	21	35	51	170	204
0.38	1301	2-Methylnonane	13	312	84	79	23	54	34	180	215
0.38	1301	3-Ethyltoluene	1	108	36	56	11	40	94	234	148
0.64	1099	2-Ethyltoluene/3-Methylnonane	24	370	105	111	29	51	77	212	300
1.24	1099	1,2,4-Trimethylbenzene/tertButylbenzene/1-Decene	93	1094	273	266	75	139	254	838	740
0.38	1301	Isobutylcyclohexane	6	147	34	34	10	31	19	115	98
0.38	1301	Decane	41	1025	251	270	90	59	30	53	722
1.00	1228	Isobutylbenzene/trans-1-Methyl-2-pentylcyclohexane	5	116	29	28	8	25	16	85	81
1.00	1228	sec-Butylbenzene	6	146	36	36	10	30	22	110	107
1.00	1228	3-Isopropyltoluene	5	160	37	35	9	20	15	85	92
0.94	1099	1,2,3-Trimethylbenzene	25	421	99	103	33	78	93	326	289
1.00	1228	4-Isopentyltoluene	6	92	24	24	8	20	9	56	63
1.00	1228	Indan	52	206	64	35	11	47	46	101	119
1.00	1228	2-Isopentyltoluene	3	78	18	17	6	20	14	68	49
1.00	1228	1,3-Diethylbenzene	6	116	23	25	7	22	37	77	59
1.00	1228	3-n-propyltoluene	13	227	52	55	19	29	17	68	155
0.81	1228	1,4-Diethylbenzene	6	301	49	60	9	23	121	123	102
1.00	1228	4-n-propyltoluene/n-Butylbenzene/1,3-Dimethyl-5-ethylbenzene	12	255	66	60	19	18	22		173
1.00	1228	1,2-Diethylbenzene	2	51	15	19	6	20	25	42	54
1.00	1228	2-n-Propyltoluene	4	200	38	44	13	21	31	52	109
1.00	1228	1,4-Dimethyl-2-ethylbenzene	10	252	53	58	22	24	22	60	163
1.00	1228	1,3-Dimethyl-4-ethylbenzene	5	106	24	24	10	17	14	37	68
1.00	1228	1,2-Dimethyl-4-ethylbenzene	10	135	29	28	12	19	16	49	81
1.00	1228	1,3-Dimethyl-2-ethylbenzene	4	210	48	54	19	45	39	166	142
0.48	1430	Undecane	20	1358	290	321	140	73	38	68	872
1.00	1228	1,2-Dimethyl-3-ethylbenzene	2	78	18	32	13	34	45	117	51
1.00	1228	1,2,4,5-Tetramethylbenzene/2-Methylbutylbenzene	10	331	65	71	30	61	43	172	187
1.00	1228	tert-Butyl-2-methylbenzene	1	59	14	17	6	8	5	28	40
1.00	1228	n-Pentylbenzene	4	148	31	32	16	20	39	50	86
0.81	1228	trans-1-Methyl-2-(4-methylpropyl)cyclopentane	2	174	37	44	15	22	23	38	110
1.00	1228	tert-Butyl-3,5-dimethylbenzene	2	189	35	35	17	16	8	37	89
1.00	1228	tert-Butyl-4-ethylbenzene	1	67	14	16	7	13	10	45	36
1.00	1228	Naphthalene	10	5610	2343	4452	895	3467	5421	4905	5006
0.62	1416	Dodecane	6	1344	259	225	126	81	44	123	663

Table 25: Pure herder combustion analysis

Volatile Organic Compounds [by GC-FID with cryogenic preconcentration, ERMS Method 4.04/*.*/*M]

* Full VOC compound list –

BOLD RED values surpass upper limit calibrations

BOLD BLUE values are below method quantification limit (MQL)

MQL	Calibration Upper Limit (ng/L)	Canister #	ng/L		
			4875	5961	5960
			HerdBase1	HerdBase2	HerdBase3
0.15	280	Ethylene	21.8	735.0	14.1
0.22	260	Acetylene	3.3	740.8	14.1
0.22	300	Ethane	6.8	107.5	5.4
0.09	420	Propene	12.5	123.1	3.1
0.14	440	Propane	69.0	126.3	8.0
0.09	420	Propyne	1.3	16.8	4.5
0.10	580	Isobutane	0.6	0.6	0.3
0.12	513	Isobutene/1-Butene	1.7	68.2	1.7
0.19	623	1,3-Butadiene		87.6	0.3
0.21	580	Butane	1.0	14.6	0.6
0.08	560	trans-2-Butene	0.1	9.5	0.2
0.12	513	1-Butyne		1.1	
0.16	560	cis-2-butene		1.2	0.2
0.19	623	1,2-Butadiene		1.1	
0.09	641	3-Methyl-1-butene			
0.24	660	2-Methylbutane	1.9	0.7	1.7
0.19	623	1,4-Pentadiene			
0.12	513	2-Butyne		0.7	
0.09	641	1-Pentene	0.4	3.9	0.2
0.09	641	2-Methyl-1-butene	0.2	8.3	0.2
0.11	660	Pentane	0.9	1.2	1.1
0.19	623	2-Methyl-1,3-butadiene	0.7	16.0	0.6
0.22	641	trans-2-Pentene	0.2	26.6	0.3
0.18	788	cis-2-Pentene		15.0	
0.09	641	2-Methyl-2-butene	0.4	1.6	0.3
0.19	623	trans-1,3-Pentadiene		4.0	
0.19	623	Cyclopentadiene	0.2	15.5	0.3
0.18	788	2,2-Dimethylbutane/cis-1,3-pentadiene	0.1	1.7	0.1
0.09	641	Cyclopentene	0.5	1.0	
0.25	770	4-Methyl-1-Pentene/3-Methyl-1-Pentene		1.2	
0.09	641	Cyclopentane	0.4	0.8	0.2
0.27	860	2,3-Dimethylbutane	1.6	1.3	1.6
0.10	860	2-Methylpentane	0.4	4.1	0.5
0.25	770	cis/trans-4-Methyl-2-pentene	0.7	2.9	1.1

0.15	860	3-Methylpentane	0.5	0.5	0.6
0.25	770	2-Methyl-1-pentene			
0.25	770	1-Hexene	0.3	6.3	
0.25	860	Hexane	0.4	24.3	0.5
0.25	770	trans-2-Hexene	0.2	3.6	
0.25	770	2-Methyl-2-Pentene		1.9	
0.25	770	trans-3-Methyl-2-Pentene		1.1	
0.25	770	cis-2-Hexene		0.5	
0.25	770	cis-3-Methyl-2-pentene	0.9	0.8	0.6
0.18	916	2,2-Dimethylpentane			
0.09	770	Methylcyclopentane	0.3	5.7	0.3
0.18	916	2,4-Dimethylpentane	0.1		0.2
0.18	916	2,2,3-Trimethylbutane	0.1	0.3	
0.09	714	Benzene	0.7	125.1	1.9
0.18	916	3,3-Dimethylpentane		0.7	0.2
0.18	840	Cyclohexane	0.2	1.6	0.3
0.10	916	2-Methylhexane	0.4	0.9	0.9
0.38	916	2,3-Dimethylpentane	0.8	0.7	0.7
0.18	840	1,1-Dimethylcyclopentane			
0.18	840	Cyclohexene		1.2	
0.12	916	3-Methylhexane	1.0	12.4	1.5
0.18	840	cis-1,3-Dimethylcyclopentane			0.1
0.12	916	3-Ethylpentane/trans-1,3-Dimethylpentane			
0.20	916	1-Heptene/trans-1,2-Dimethylcyclopentane		3.6	
0.17	1045	2,2,4-Trimethylpentane	0.4	0.5	0.4
0.20	916	trans-3-Heptene	0.1	0.2	
0.20	916	Heptane	0.3	0.4	0.5
0.20	916	cis-2-Heptene		0.2	
0.20	916	trans-2-Heptene	0.6	0.2	0.2
0.20	916	cis-3-Heptene			
0.15	980	Methylcyclohexane/2,2-Dimethylhexane	0.4	0.4	0.2
0.14	1045	2,5-Dimethylhexane/Ethylcyclopentane			
0.14	1045	2,4-Dimethylhexane/2,2,3-Trimethylpentane		0.2	
0.14	1045	3,3-Dimethylhexane/cis-trans-cis-1,2,4-Trimethylcyclopentane	0.5	24.2	0.1
0.15	980	cis-trans-cis-1,2,3-Trimethylcyclopentane	0.4		0.3
0.14	1045	2,3,4-Trimethylpentane	0.3		
0.21	919	Toluene	2.1	14.5	2.6
0.14	1045	2,3-Dimethylhexane		0.2	
0.14	1045	2-Methyl-3-Ethylpentane			
0.10	950	2-Methylheptane/1-Methylcyclohexene	0.2	0.2	0.1
0.10	950	4-Methylheptane/3-Methyl-3-Ethylpentane	0.3	0.2	0.1
0.10	950	3,4-Dimethylhexane			
0.12	1045	3-Methylheptane/3-Ethylhexane	0.1		
0.15	980	cis-cis-trans-1,2,4-Trimethylcyclopentane/cis-1,3-Dimethylcyclohexane	0.8	1.1	0.3
0.15	980	trans-1,4-Dimethylcyclohexane	0.2		
0.11	1045	2,2,5-Trimethylhexane		35.5	0.4
0.11	1045	1-Octene	0.3	2.4	
0.15	980	1-Ethyl-1-methylcyclopentane			
0.11	1045	Octane/trans-1,2-Dimethylcyclohexane	0.7	0.3	1.3
0.11	1045	trans-2-Octene	0.7		0.2
0.15	980	cis-cis-cis-1,2,3-Trimethylcyclopentane			
0.11	1045	2,2,4-Trimethylhexane			

0.11	1045	cis-2-Octene/Isopropylcyclopentane			
0.11	1045	2,3,5-Trimethylhexane			
0.11	1045	2,4-Dimethylheptane	0.1		0.3
0.11	1045	2,6-Dimethylheptane/cis-1,2-Dimethylcyclohexane	2.8		
0.15	980	n-Propylcyclopentane			
0.15	980	cis-cis-cis-1,3,5-Trimethylcyclohexane			
0.11	1045	2,5-Dimethylheptane/3,5-Dimethylheptane			
0.11	1045	3,3-Dimethylheptane			
0.15	980	1,1,4-Trimethylcyclohexane		0.5	
0.28	971	Ethylbenzene	0.2	2.5	0.5
0.15	980	cis-trans-trans-1,2,4-Trimethylcyclohexane			
0.09	1280	2,3-Dimethylheptane			
1.07	971	m&p-Xylene/3,4-Dimethylheptane	1.0	7.0	1.9
0.09	1280	2-Methyloctane	2.6		
0.09	1280	3-Methyloctane			
1.30	857	Styrene/cis-trans-cis-1,2,4-Trimethylcyclohexane	0.5	1.9	0.2
0.09	1280	3,3-Diethylpentane			0.7
0.35	883	o-Xylene	0.4	0.6	0.6
0.09	1280	1-Nonene/1,1,2-Trimethylcyclohexane		1.9	
0.09	1280	trans-3-Nonene			
0.09	1280	cis-3-Nonene/Isobutylcyclopentane		0.4	0.3
0.09	1280	Nonane	0.4		
0.09	1280	trans-2-Nonene			
0.09	1280	cis-2-Nonene	0.2	0.2	
0.28	1099	Isopropylbenzene		0.2	
0.09	1280	2,2-Dimethyloctane		0.2	
0.09	1280	Isopropylcyclohexane	0.2		
0.09	1280	n-Butylcyclopentane	1.1	2.0	1.5
0.09	1280	3,3-Dimethyloctane	0.4	0.3	0.2
0.47	1099	n-Propylbenzene	0.4	0.2	0.2
0.46	1099	3-Ethyltoluene	0.6	0.5	0.5
0.85	1099	4-Ethyltoluene/2,3-Dimethyloctane	0.3	0.4	0.4
0.52	1099	1,3,5-Trimethylbenzene	0.2	0.3	0.2
0.38	1301	2-Methylnonane	2.3	0.1	0.1
0.38	1301	3-Ethylloctane		0.2	
0.64	1099	2-Ethyltoluene/3-Methylnonane	0.3	0.2	0.2
1.24	1099	1,2,4-Trimethylbenzene/tertButylbenzene/1-Decene	0.5	3.9	0.8
0.38	1301	Isobutylcyclohexane			
0.38	1301	Decane	0.9	0.4	0.5
1.00	1228	Isobutylbenzene/trans-1-Methyl-2-pentylcyclohexane			
1.00	1228	sec-Butylbenzene			
1.00	1228	3-Isopropyltoluene	0.3	0.3	0.2
0.94	1099	1,2,3-Trimethylbenzene	0.2		0.3
1.00	1228	4-Isopentyltoluene	0.1		0.2
1.00	1228	Indan	1.2	0.8	0.5
1.00	1228	2-Isopentyltoluene			
1.00	1228	1,3-Diethylbenzene			0.7
1.00	1228	3-n-propyltoluene			
0.81	1228	1,4-Diethylbenzene	0.4		0.3
1.00	1228	4-n-propyltoluene/n-Butylbenzene/1,3-Dimethyl-5-ethylbenzene	0.3		
1.00	1228	1,2-Diethylbenzene	0.1		
1.00	1228	2-n-Propyltoluene	0.2		0.1

1.00	1228	1,4-Dimethyl-2-ethylbenzene	0.2	0.1	0.2
1.00	1228	1,3-Dimethyl-4-ethylbenzene	0.2	0.2	
1.00	1228	1,2-Dimethyl-4-ethylbenzene	0.1		0.1
1.00	1228	1,3-Dimethyl-2-ethylbenzene		1.1	
0.48	1430	Undecane	0.7	0.5	0.7
1.00	1228	1,2-Dimethyl-3-ethylbenzene			
1.00	1228	1,2,4,5-Tetramethylbenzene/2-Methylbutylbenzene	0.3		0.3
1.00	1228	tert-Butyl-2-methylbenzene			
1.00	1228	n-Pentylbenzene		0.5	
0.81	1228	trans-1-Methyl-2-(4-methylpropyl)cyclopentane	1.5		0.2
1.00	1228	tert-Butyl-3,5-dimethylbenzene			0.3
1.00	1228	tert-Butyl-4-ethylbenzene	0.2		
1.00	1228	Naphthalene	0.5	3.2	0.3
0.62	1416	Dodecane	0.6	0.2	0.9

6. CONCLUSIONS

6.1 Research on Windows of Opportunity for Herder Use

- In general the OP-40 was slightly more effective with all four fresh crudes than the TS6535.
- The initial herded thickness achieved is a function of both herder and crude type. For fresh ANS crude OP-40 could thicken a slick from 0.6 mm to 2.9 mm while TS6535 could achieve only 0.7 to 2.1 mm. OP-40 herded fresh Endicott slicks from 2.2 mm to 5.1 mm and TS6535 could achieve 2.5 mm to 4.9 mm. OP-40 herded fresh Terra Nova slicks from 2.5 mm to 4.7 mm and TS6535 achieved 2.6 mm to 4.2 mm. OP-40 herded fresh Grane crude from 1.9 mm to 7.9 mm and TS6535 achieved 2.2 mm to 7.2 mm.
- The thickness of slicks herded with OP-40 decreased slowly over the one hour tests (i.e., the slicks spread slowly). The thickness of slicks herded with TS6535 declined less slowly, or not at all.
- Evaporated crude oil is herded to greater thickness than fresh crude, providing the oil can still flow at the water temperature.
- Herders can contract slicks with 20% emulsified water content (the maximum ignitable), but not slicks with 50% water content.
- Herders can still contract oil slicks at temperatures up to 8° - 10 °C below the oils' pour point. Wave action seems to help with this.
- The presence of slush ice restricts both oil spreading and herder effectiveness. In 30% slush ice cover the herders can still function, but in 100% slush ice cover the oil does not spread and the herder is prevented from reaching the slick. In general, the OP-40 herder worked more effectively than the TS6535 in slush ice.
- The simulated wave action in the Dynamic Film Performance apparatus generally reduced herder effectiveness with the low Pour Point ANS crude compared to calm conditions, but increased herder effectiveness with the high Pour Point Terra Nova crude.
- During test burns, the ignited slicks restrained by herders would spread slightly during burning, then contract again as the flames extinguished. The burn efficiencies were slightly lower than burns of similar diameter and thickness in a metal containment ring. The burns of slicks restrained with OP-40 resulted in slightly higher removal efficiencies than those restrained by TS6535. The ANS crude had higher burn efficiencies than the Grane crude.
- Herded slicks in gentle waves in a wave tank tended to break up into smaller and smaller slicklets as wave period decreased. Once breaking waves were generated, the herder monolayer was quickly disrupted and the slicks spread and sheened.

6.2 Research on Fate and Effects of Chemical Herders

6.2.1 Burning Experiments at DTU

- In general, ANS and Grane crude oils achieved relatively low burning efficiency of 37% and 21-26% respectively, which is in agreement with results from similar studies where similar amount of ANS was used. These efficiencies are lower than those measured in the SL Ross experiments because the volumes of oil used were smaller.

- As was noted in the SL Ross test burns, the burning efficiencies achieved by Grane are lower than those achieved by ANS, due to differences in the oil properties.
- The ANS and Grane 25% water-in-oil emulsions resulted in much higher burning efficiencies than those for fresh crude oils. More intense boilover was observed with sharp rise in flame heights during the burning of the emulsified oil slicks, it was estimated that between 12-18% and 18-28% is burned owing to intense boilover tendency for ANS and Grane respectively with regard to the fresh crude oils.
- For most of the small laboratory experiments the herding agent OP40 outperformed TS6535.
- The TS6535 did not achieve as thick slicks as OP40, especially for Grane, and this is most likely due to sheen formation, which might have a buffering effect for the hydrocarbon based herder. In addition, two other possibilities may explain this poor performance, either the ANS crude differs significantly from previous samples, or the batch of TS6535 was not properly formulated.
- The greatest slick thicknesses were achieved when the water was pre-treated with the herding agents. This is presumably due to an increased contact surface for the crude oil with the monolayer. Then TS6535 was indeed able to thicken both crude oils with slick thickness above 3 mm, this results supports the sheen formation hypothesis. The possible buffer effect of sheen formations should be further studied since it may contribute to the TS6535's poor performance.
- In the long-term laboratory experiments, the monolayer produced by OP40 seemed to lose its surface tension properties after 60 minutes, after which point the effect of the herder declined and after 6-8 hours the oil slick thickness returned to initial conditions. ThickSlick 6535, on the other hand, could keep ANS and Grane oil slicks herded for up to 100 and 350 hours, respectively.

6.2.2 *Physical Fate of Herder during Burning*

- Small concentrations of herders were found in the water column samples taken at the end of the experiment.
- For the post burn samples, water surface and water column, the concentrations are highest when the test oil is emulsified. This was noted for both oil types.
- Samples taken directly under the oil slick had overall higher concentration, in particular for OP-40.
- Generally, after burning, the herder was mainly found on the water surface, though reduced in amount compared to pre burning.
- The herders were able to re-thicken the oil after extinction.
- The decaying effectiveness of the herders with time is ascribed to be a combination of different processes: evaporation, dissolved/entrained into the edge of the oil slick and a minor dissolution/dispersion into the water.

6.2.3 *Toxicity and Bioaccumulation of Herders in High Arctic Copepod and Biodegradation of Herders in Arctic Surface Waters*

- These studies provide basic general knowledge about the inherent properties of the herders that could be useful in a subsequent risk assessment. The tests were conducted according to OECD 309 guideline and with Arctic conditions and organisms and standard test durations.

- The effect of dissolved herders on behaviour and mortality on *Calanus hyperboreus* was observed over a period of 25 days. A distinct mortality was seen at the highest test concentrations of the herders. After 1 day 100% mortality was seen at 600 mg/L TS653. Markedly sub-lethal effect (very slow moving animals) was seen after 48 hours exposure in concentrations of 12.5 mg/L and 60 mg/L TS6535. More than 90% mortality was subsequent seen after 25 days at 60 mg/L TS6535. Corresponding 100% mortality was seen at 12.5 and 60 mg/L OP-40 and sub-lethal effect after 48 hours exposure in concentrations of 2.5 mg/L OP-40. More than 90% mortality was subsequent seen after 25 days at 2.5 mg/L OP-40. To put these results in context, it should be noted that all of these effect concentrations of dissolved herders in water are several orders of magnitude greater than the herder concentrations measured underneath the test slicks in experimental burns in the lab.
- The results showed that the degradation of OP-40 was insignificant or low over 28 days in Arctic seawater. TS6535 disappeared quickly in the test bottles probably due to rapidly biodegradation.
- The results indicate that OP-40 may bioaccumulate and TS6535 may not bioaccumulate in the high Arctic copepods.
- It should be noted that recovery rates are low and particularly for TS6535 was difficult to measure and that some uncertainty must be related to the results are uncertain. The low recovery can be attributed to the due to the poor solubility of the herders in water and that herders have a great tendency to be caught in the surface film, as well as degrade fast (TS6535). However, it must be noted that the studies on herders are complicated by the poor solubility and derived poor distribution of herders in water.

6.3 Impacts of Herders on Feathers from Arctic Sea Birds

- For most of the exposure experiments the barbule Amalgamation Index decreased by decreasing the concentrations.
- No Observed Effect Concentration (NOEC) and the related No Observed Effect Slick Thickness (NOEST) were calculated. Thick-billed Murre feathers seem less sensitive than Common Eider feathers in the combined experiments with both crude oil and OP-40 results in the lowest effect thicknesses.
- Both herders significantly increase the feather weight and Amalgamation Index (AI).
- The concentrations of herders included 150 $\mu\text{L}/\text{m}^2$, 20 $\mu\text{L}/\text{m}^2$ and 1-3 $\mu\text{L}/\text{m}^2$. The 150 $\mu\text{L}/\text{m}^2$ is the recommended application dosage that must be applied to contract the oil in the field. This dosage will result in a monolayer of herder being fed, as it spreads out, from droplets of surplus herder, until the herder has spread out completely. The 20 $\mu\text{L}/\text{m}^2$ is the minimum dosage needed to contract the oil to ignitable thicknesses, determined from laboratory experiments. This dosage will also result in a monolayer and droplets of surplus herder, until the herder has spread out completely. The 1-3 $\mu\text{L}/\text{m}^2$ is the estimated dosage that is expected to result in a monolayer without the droplets of surplus of herders. It is the monolayers that most likely are to be found in the majority of the herder "slick". The feathers exposed to 150 $\mu\text{L}/\text{m}^2$ and 20 $\mu\text{L}/\text{m}^2$ of OP-40 sank immediately (< seconds) after they came in contact with herder.
- The OP-40 monolayer experiments with a monolayer dosage (1 $\mu\text{L}/\text{m}^2$) showed that the feather did not sink.

- The feathers exposed to 150 $\mu\text{L}/\text{m}^2$, 20 $\mu\text{L}/\text{m}^2$ and 3 $\mu\text{L}/\text{m}^2$ TS6535 did not sink, but slowly absorbed water.

6.4 Smoke Plume Analysis

- The use of both herders did not have a negative impact on the primary BTEX compounds analysed in the smoke plumes.
- The chromatograms did not show obvious signs of herder
- No significant increase in the products of combustion were detected in the smoke from in situ burning experiments using herded oil slicks.

7. RECOMMENDATIONS

- Care must be taken in the production and storage of TS6536. The batch of TS6535 provided to CRREL was not as effective as the others (SL Ross and DCE) and was either not properly formulated or mixed. After being warmed and shaken before each test, the performance of this batch of TS6535 seemed to improve.
- Additional large-scale field testing in actual drift ice conditions with both herders is required to fully define their Window of Opportunity.
- Additional research is suggested, focusing specifically on the analysis of possible siloxanes being formed at very low concentrations during the combustion of oil contained by the OP-40 herder. Given the low application rate of the herder and the dilution effect of the relatively large amount of oil being combusted, specialized monitoring and/or analytical equipment would be needed to detect the presence of such compounds that were beyond the scope of this project.
- Further studies are recommended to more deeply examine the findings in the report for the herder fate.
- Biodegradation tests of TS6535 should be done that focus on the first hours and days.
- The long term effects from herders on seabirds should be studied.
- Investigate if the effects found from oil /dispersant exposure could be transferred to the effects from herders.

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APPENDIX 1 – MSDS FOR TS 6535

APPENDIX 2 – MSDS FOR OP-40

APPENDIX 3 – OECD 309

